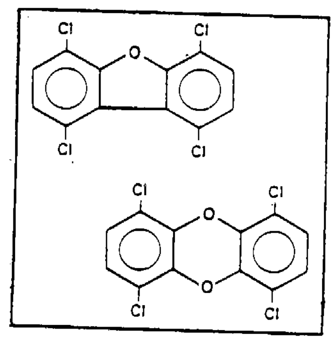
Document No. P-E509-400-01

Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin

Phase I Summary Report



Prepared for:

California Air Resources Board
Sacramento, CA

June 1987

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environmental and engineering excellence

July 1, 1987

Ms. Laura R. Kinney
Contract Administrator
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Subject: Phase I Summary Report-Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin (ERT Project E-509-400 CARB Agreement # A6-100-32)

Dear Ms. Kinney:

Enclosed please find 20 copies of the Phase I Summary Report entitled Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin. This document constitutes the Interim Report for all Phase I activities as specified in the CARB Agreement with ERT (# A6-100-32). As such it contains the results of all activities required as part of the Phase I scope of work including the following: literature survey, site selection, and sampling and analysis plan.

The enclosed document was prepared under the direction of Mr. Joseph Pantalone, the CARB Program Manager, who will process the report through the CARB Review process as appropriate. It is ERT's understanding that CARB will review the enclosed document and provide specific additional guidance it deems appropriate prior to providing approval to proceed with the Phase II scope of work.

Should you or any of the CARB Review Staff require any additional information, or should you have any questions upon receipt of the plan, please do not hesitate to contact me or Dr. Alan Lloyd in our Newbury Park, California office. I look forward to hearing from you.

Sincerely,

Gary T. Hunt

Gary T. Hunt
Program Manager
Manager Air Toxics Monitoring and Chemistry

GTH/rab

cc: J. Pantalone/ CARB
A. Lloyd/ ERT, Newbury Park
M. Lundgren/ ERT
P. Fennelly/ ERT
J. Spaulding/ ERT

DISCLAIMER

The statements and conclusions in this report are those of the Contractor and not necessarily those of the State Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be constructed as actual or implied endorsement of such products.

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1. INTRODUCTION

1.1 Program Background/Overview

The California Air Resources Board (CARB) has designated certain chlorinated dibenzofurans and dibenzodioxins to be toxic air contaminants subject to review and possible regulation in accordance with AB 1807 (Section 39650, et seq. of the California Health and Safety Code; Assembly bill 1807, Tanner, 1983). In response, the CARB has identified a requisite for the collection of background data to determine existing population exposures, as well as establish a "baseline" data base of PCDD/PCDF concentrations in ambient air in the South Coast Air Basin. It is anticipated that such a data base will be suitable for the assessment of what impacts, if any, the addition of selected combustion sources of the South Coast Air Basin will have on existing concentrations of PCDDs/PCDFs.

As a result, ERT, A Resource Engineering Company, has been retained by CARB to conduct a "Study of Ambient Concentrations of Chlorinated Dibenzodioxins and Dibenzofurans in Urban Areas of the South Coast Air Basin." The purpose of this project is to determine baseline qualitative and quantitative data on the concentrations of certain chlorinated dioxins and furans in ambient air. The specific components of interest include those isomers (Cl_4-Cl_7) of polychlorinated dibenzodioxins and polychlorinated dibenzofurans that are chlorine substituted at the 2, 3, 7, 8 positions. This listing includes the 15 congeners shown in Table 1-1.

1.2 Program Purpose and Objectives

The primary purpose and objectives of the proposed monitoring program are as follows:

TABLE 1-1

LISTING OF PCDD/PCDF ISOMERS SELECTED FOR SAMPLING AND ANALYSIS IN THE SOUTH COAST AIR BASIN

PCDD Isomers	PCDF Isomers
2,3,7,8 TCDD	2,3,7,8 TCDF
1,2,3,7,8 PeCDD	1,2,3,7,8 PeCDF
1,2,3,6,7,8 HxCDD	2,3,4,7,8 PeCDF
1,2,3,7,8,9 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,4,7,8 HxCDD	1,2,3,7,8,9 HxCDF
1,2,3,4,6,7,8 HpCDD	1,2,3,4,7,8 HxCDF
	2,3,4,6,7,8 HxCDF
	1,2,3,4,6,7,8 HpCDF
	1,2,3,4,7,8,9 HpCDF

- Determine, through a program of field sampling and laboratory analysis, the ambient concentrations of chlorinated dioxins and furans in the South Coast Air Basin, with particular attention to the following: 1) areas of high population density, 2) areas where selected types of incinerators and combustion sources are located which presently burn chlorine containing wastes and may give rise to PCDDs/PCDFs, and 3) areas in which such incinerators are proposed for the future.
- It is anticipated that the data obtained through this study will be used by CARB and others for both health assessment purposes and to compare current concentrations with future concentrations.

1.3 Program Scope

The program purpose and objectives described above will be accomplished in two discrete phases as follows:

<u>Phase I</u>

- ERT will conduct a literature search to identify information on the sources, formation, distribution, occurrences, and atmospheric chemistry (transport and fate) of chlorinated dibenzodioxins and dibenzofurans. This information will augment the data in the report that CARB staff prepared for the Scientific Review Board during the evaluation of whether to classify PCDDs and PCDFs as toxic pollutants;
- Select sites in the South Coast Air Basin which meet the objectives of the program stated above;

- Design a sampling and analytical plan to be employed at these sites. This will include the design of a comprehensive QA/QC plan for sampling and analysis; and
- Prepare an interim report of Phase I activities.

<u>Phase II</u>

Phase II of the program will be accomplished in three major tasks:

- The acquisition of at least 50 ambient samples and their subsequent analysis:
- The development and implementation of an extensive quality assurance plan conforming to CARB and EPA requirements; and
- The delivery of a Draft Final and Final Report to the CARB. This report will include the information contained in the Phase I interim report and is expected to be a comprehensive document on the subject.

1.4 Phase I Interim Report Organization

The document to follow constitutes the Phase I Interim Report and as such contains the results of all Phase I activities. In accordance with the scope of work it has been divided into discrete sections as follows:

- Literature Review - Section 2
- Monitoring Site Selection Process - Section 3
- Monitoring Network Design - Section 4
- Meteorological Monitoring - Section 5
- Sample Collection Procedures - Section 6
- Evaluation Criteria for the Selection of Field Samples for Analysis - Section 7

- Analytical Procedures - Section 8
- Quality Assurance/Quality Control - Section 9
- Data Interpretation - Section 10
- Bibliography - Section 11

Appendices to the body of the report contain detailed operating procedures for meteorological monitoring, sample collection, sampler calibration, sorbent pretreatment, and sample analyses.

2. LITERATURE REVIEW

2.1 Introduction

An integral component in the project Work Scope consisted of the conduct of a comprehensive literature search on the formation and atmospheric behavior of PCDDs/PCDFs. It was envisioned that this literature survey would expand upon information contained in a CARB Technical Support Document entitled "Report to the Scientific Review Panel on Chlorinated Dioxins and Dibenzofurans" focusing on chlorinated dioxin and dibenzofuran sources, emissions and public exposure[1]. Based upon our review of this document and ERT's understanding of the objectives of the CARB it was further determined that the literature survey should, at a minimum, focus on the following:

- Identify potential sources of PCDDs/PCDFs in the South Coast Air Basin. Particular emphasis was placed on combustion source categories identified as known PCDD/PCDFs emission sources. Additional consideration was also given to contaminated area sources that were identified as potential fugitive emission sources of PCDDs/PCDFs.
- Compilation of an ambient air quality data base comprised of all existing measurements of PCDDs/PCDFs in ambient air worldwide. This exercise will provide an additional "benchmark" for subsequent evaluation of the data to be collected as part of the present program.

2.2 Information Sources Cited

A multi-faceted approach was employed in the collection, compilation, and evaluation of the requisite data. This included but was not limited to the following generic types of information:

- Review of existing literature files
- Computerized searches of open literature employing "Key Word" index approach.
- Interaction with active research community.

Further details on each of these are provided below.

2.2.1 Existing Literature Files

ERT maintains a vast library of in-house reference materials on the subject of PCDDs/PCDFs in the environment. These consist of a series of literature compilations or bibliographies as well as individual periodicals or technical symposia citations. A listing of some of the more noteworthy bibliographies that were reviewed as part of the literature survey are listed in Table 2-1. Specific citations were identified in each of these documents and reviewed to assess their relevance to the aforementioned program objectives. Pertinent citations were then categorized for inclusion in the appropriate portion of the literature review discussion to follow commencing in Section 2.3.

2.2.2 Computerized Searches Employing "Key Word" Index

ERT made use of available in-house on line search regimes to identify additional literature citations not contained in the aforementioned bibliographies. The computerized system provides indepth subject retrieval of relevant journal articles, conferences, reports, theses and books. A "key word" index tailored to the program objectives was created and subsequently used to retrieve pertinent citations both on a retrospective basis as well as a "real time" or ongoing basis. A copy of the actual key word index employed in this manner is provided in Table 2-2. Abstracts of all articles were then reviewed and copies of relevant articles were retrieved for further review and inclusion in the appropriate portion of the literature discussion to follow.

TABLE 2-1

MAJOR BIBLIOGRAPHIES REVIEWED AS PART OF THE LITERATURE SURVEY

- National Dioxin Study Tier IV Combustion Sources - Final Literature Review June 1986 (EPA 450/4-84-014J)

- ASME Bibliography on Dioxins 2nd Edition April 1986 Prepared by American Society of Mechanical Engineers Dioxins Committee

- Technical Support Document Report on Chlorinated Dioxins and Dibenzofurans Part A. A Review of Chlorinated Dioxin and Dibenzofuran Sources, Emissions and Public Exposure. Prepared by CARB, Feb. 1986.

TABLE 2-2

SAMPLE KEY WORD INDEX

SDI006 SUMMARY

User:004756 , File 6
TITLE:DIALOG 2 SDI PRINTS for UD=8707

SDI006, UD 8707, SER. NUH5

File(s) searched:

File 6:NTIS - 64-87/ISS07 (COPR. 1987 NTIS)

Sets selected:

Set	Items	Description
1	26	AIR POLLUTION/DE
2	0	AIR POLLUTION SAMPLING/DE
3	1	AIR SAMPLING/DE
4	0	INCINERATION/DF
5	0	INCINERATORS/DF
6	23	SOURCES/DF
7	4	AMBIENT(W)AIR
8	53	1 OR 2 OR 3 OR 4 OR 5 OR 6 OR 7
9	0	** Invalid select command ** # URBAN(W)
10	1	PARTICULATES/DF
11	3	FLUE GAS/DE
12	0	FLUE BASES/DE
13	0	WASTE GASES/DE
14	4	9 OR 10 OR 11 OR 12 OR 13
15	56	8 OR 14
16	10	PESTICIDES/DF
17	4	SOLVENTS/DF
18	0	CHLORINATED(W)PESTICIDE? ?
19	1	CHLORINATED HYDROCARBONS/DE
20	0	CHLOROHYDROCARBONS/DF
21	0	CHLOROCARBON? ?
22	3	POLYCYCLIC AROMATIC HYDROCARBONS/DE
23	18	16 OR 17 OR 18 OR 19 OR 20 OR 21 OR 22
24	0	POLYNUCLEAR AROMATIC HYDROCARBONS/DE
25	3	AROMATIC POLYCYCLIC HYDROCARBONS/DE
26	1	POLYCHLORINATED BIPHENYLS/DE
27	0	** Invalid select command ** # BIPHENYL/CHLORO/DE
28	0	** Invalid select command ** # DIOXIN/TETRACHLORO-DIBENZO/DE
29	0	TETRACHLORO(W)DIBENZO(W)FURAN
30	4	24 OR 25 OR 26 OR 27 OR 28 OR 29
31	0	POLYCHLORINATED(W)DIBENZO(W)DIOXIN
32	0	POLYCHLORINATED(W)DIBENZO(W)FURAN
33	0	CHLORO(W)DIBENZO(W)DIOXIN
34	0	ASKAREL? ?
35	0	DIBENZO(W)DIOXIN
36	0	DIBENZO(W)FURAN
37	2	TETRACHLORODIBENZO?
38	1	POLYCHLORINATED(W)DIBENZO?
39	2	31 OR 32 OR 33 OR 34 OR 35 OR 36 OR 37 OR 38
40	1	PCDD? ?
41	3	DIOXIN? ?
42	0	FURAN
43	1	PCDF? ?
44	0	TCDF? ?
45	3	40 OR 41 OR 42 OR 43 OR 44
46	23	23 OR 30 OR 39 OR 45
47	5	15 AND 46

Prints requested ('*' indicates user print cancellation) :

Date	Time	Description
20mar	02:28EST	PR 47/5/1-25 (items 1-5)

Total items to be printed: 5

001016

DIALOG INFORMATION SERVICES, INC

2.2.3 Interactions with Active Technical Community

A third and perhaps the most valuable information gathering tool employed by ERT consisted of direct telephone contact with a preselected listing of members of the technical community actively involved in the sources, distribution, occurrences, transport and fate of PCDDs/PCDFs in the environment. This included a telephone survey of members of the regulatory community (e.g., municipalities, state agencies, U.S. EPA), academia and others such as vendors of municipal refuse incineration systems. The latter group for instance commonly deals with PCDDs/PCDFs as a requisite part of the permitting process.

As it turns out, this exercise was invaluable in identifying up to date information on ambient concentrations of PCDDs/PCDFs which is not generally available at this time in the open literature. This information, by the way, provides the basis for the discussion on atmospheric concentrations of PCDDs/PCDFs contained in Section 2.5.

2.3 PCDDs/PCDFs in Stationary Combustion Source Emissions

In December of 1983 the Environmental Protection Agency formulated a National Dioxin Strategy whose primary charge was to "study the nature and extent of environmental contamination of 2,3,7,8-TCDD and the associated risks to humans and the environment"[2].

In the process of providing a manageable and yet logical approach to the dioxin dilemma, EPA identified a series of source categories or Tiers which were thought to constitute the major potential sources of PCDDs/PCDFs in the environment. These seven categories, or Tiers, consisted primarily of area sources where PCDDs/PCDFs may be deposited as a result of the production, handling, storage and/or disposal of 2,4,5-trichlorophenol and 2,4,5-TCP related products.

Particular attention was focused as well on combustion point sources where the incineration or thermal disposal of wastes contaminated with PCDDs/PCDFs or their chlorinated precursors might give rise to 2,3,7,8-TCDD in flue gas emissions or pollution control residuals (e.g. flyash). As a consequence of this directive, the Tier IV work group identified a listing of combustion source categories that posed the greatest potential for releases of chlorinated dioxins (PCDDs). A preliminary listing of these source categories was created at the outset of the Tier IV program and later refined as a result of actual test data collected during the conduct of the Tier IV investigation. A listing of the Tier IV source categories identified by EPA as potential sources of PCDDs is provided in Table 2-3. This listing also includes the source rankings (A-D) and ranking criteria as they stood at the completion of the Tier IV test program.

Source Categories within the State of California

The California Air Resources Board (CARB) as part of its continuing investigation into the sources of PCDDs/PCDFs within the State of California compiled an inventory of those point sources within each of the aforementioned categories that constitute potential sources of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). A listing of these source categories including both combustion point sources and area sources as they appeared in the CARB technical support document is provided in Table 2-4. As shown, numbers of operational and proposed facilities within each source category are provided as well as an approximate PCDDs/PCDFs emissions estimate (high, low, unknown) for each.

ERT employed this information in an attempt to select those source categories that posed the greatest potential for contributing to the existing atmospheric burden of PCDDs/PCDFs. More specifically, those source categories which contained the greatest number of operational and proposed

TABLE 2-3

COMBUSTION SOURCE CATEGORIES IDENTIFIED BY THE EPA AS POTENTIAL SOURCES OF CHLORINATED DIOXINS NATIONAL DIOXIN STRATEGY - TIER IV FINAL COMBUSTION SOURCE RANKINGS[2]

Rank A
- Sewage Sludge Incinerators
- Black Liquor Boilers

Rank B
- Industrial Incinerators
- Wire Reclamation Incinerators
- Carbon Regeneration Furnaces
- Secondary Metal Blast Furnaces
- Wood-Fired Boilers
- Drum and Barrel Reclamation Furnaces

Rank C
- Mobile Sources
- Wood Stoves
- Spreader-Stoker Coal Fired Boilers
- Commercial Boilers Burning Chlorinated Organic Wastes
- Lime Kilns
- Cement Kilns
- Hazardous Waste Incinerators
- Hospital Waste Incinerators
- Apartment House Incinerators
- Charcoal Manufacturing Operations
- Open Burning

Rank D
- Municipal Waste Incinerators
- Commercial Waste Boilers

Footnotes:

Rank A - Large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have the highest potential to emit TCDD.

Rank B - Small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have a high potential to emit TCDD.

Rank C - Source categories less likely to emit TCDD.

Rank D - Source categories that have already been tested three or more times.

TABLE 2-4

POTENTIAL CHLORINATED DIOXIN AND DIBENZOFURAN SOURCE CATEGORIES IN CALIFORNIA[1]

Source Category	Operational In Calif.	Proposed for Calif.	Estimate of Relative Emissions[1]
Point Sources			
Municipal Waste Incinerators and RDF Boilers	1	35	High
Commercial Waste Oil Burners	30 +	ND	Unknown
Hazardous Waste Incinerators	17	3	Low
Industrial Boilers Cofiring Wastes	0	0	Unknown
Wire Reclamation Incinerators	76 [2]	ND	Unknown
Sewage Sludge Incinerators	8	ND	Unknown
Wood/Bark Boilers	59	ND	High [3]
Black Liquor Boilers	4	0	Unknown
PCP Sludge Incinerators	ND	ND	High
Cement Kilns Cofiring Wastes	1	1	Low
Hospital Incinerators	311 [2]	ND	Unknown
Sawmills[4]	86	ND	High [3]
Area Sources			
Mobile Sources	NA		Unknown
Wood Stove/Fireplaces	NA		Unknown
Forest Fire/Agricultural Burning	NA		Unknown

ND - no data
NA - not applicable

1. This is a qualitative assessment of the expected emissions relative to the other source categories listed.
2. Statewide number estimated from data supplied by San Diego Air Pollution Control District and South Coast Air Quality Management District.
3. When burning wood treated with chlorophenol, otherwise these are rated as low.
4. Most sawmills have the capability to incinerate some or all of the woodwaste produced at the facility. A wood/bark boiler may be used at a sawmill to incinerate process wastes. This source category may overlap other source categories listed in the table.

facilities in combination with a "high" CARB and/or EPA ranking were selected for further discussion. These include the following source categories which are treated in greater detail in the discussion to follow:

- Resource recovery facilities - municipal waste incinerators.
- Sewage sludge incinerators.
- Hospital incinerators.
- Wire reclamation incinerators.

Based upon the aforementioned criteria in combination with the available literature data, it is ERT's opinion that the above source categories be given primary consideration in the subsequent portions of the literature review.

2.3.1 Resource Recovery Facilities

Since 1978 when TCDD's were detected in the emissions from the Hempstead, NY municipal waste incinerator, this source category has received considerable attention in the United States. While generally receptive to the need for new solid waste disposal methods, the public has become increasingly concerned with resource recovery facility operations, particularly emissions. Emissions have become the most sensitive of these facilities' permitting issues and a number of test programs have been completed or are ongoing to adequately assess the question of toxic emissions, particularly PCDD's and PCDF's.

Resource Recovery facilities can be broadly classified as one of three types. The majority of waste in North America is processed through mass-burn units, where waste is burned continuously over a series of grates. A smaller number of units are classified as refuse derived fuel (RDF) units, where the waste is processed into a more readily combusted fuel by shredding and metal and glass removal prior to incineration. Controlled air systems employ a two chamber combustion system and burn untreated waste on a batch cycle. The distinction between systems types is made because each design is sufficiently different to warrant breaking the dioxin test data into separate categories.

Table 2-5 and Figure 2-1 summarizes the information available in the open literature[3-9] on North American resource recovery facility emissions. Figure 2-2 summarizes the congener distribution by facility types. The hexa- and penta-dioxin homologues predominate, while the tetra- and penta-furan congeners are the most common. Figure 2-2 also demonstrates the differences in congener distribution for the three technologies. Finally, Table 2-5 and Figure 2-2 illustrate the marked differences in congener percent distributions between individual facilities within a given technology. These sources were assigned Rank D status in the Tier 4 study.

2.3.2 Sewage Sludge Incinerators

Recent estimates by the Environmental Protection Agency indicate that there are approximately 200 municipal sewage sludge incinerators presently in operation in the United States[10]. CARB statistics indicate that a number of such facilities are presently in operation in the State of California[1], 2 of which are situated in the South Coast Air Basin (one in the vicinity of the Gardena/Redondo Beach area and a second in the coastal community of El Segundo).*

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* Actual locations of sewage treatment facilities in the South Coast Air Basin are provided in the map contained in the rear pocket of this report entitled "Identified Resource Recovery Facilities in the South Coast Air Basin" (Exhibit 1).

TABLE 2-5

SUMMARY OF RESOURCE RECOVERY FACILITY DATA

Facility	PCDD EMISSIONS (ng/M3) T3CDD	T4CDD	2,3,7,8 T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	TOTAL CDD	PCDF EMISSIONS (ng/M3) T3CDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	TOTAL CDF	TOTAL PCDD + PCDF	REFERENCE
Mass Burn Facilities																	
Westchester, NY		2.11	0.21	2.11	2.88	4.10	6.57	17.76		22.20	12.95	13.39	7.78	0.28	56.60	74.36	NYS/DEC (1986)
Chicago NW, IL	12.67	6.27	4.33		16.33	7.57	2.53	32.70	300.00	89.67		62.00	7.47	0.60	159.74	192.44	Haile (1983)
Hampton, VA	46.00	309.25		900.38	659.75	493.25	128.50	2571.13	1992.40	1506.50	4308.88	886.25	534.63	37.13	7273.38	9844.50	Haile (1984)
USA, (Mayport)		3.57	1.67					3.57		21.03					21.03	24.60	Higgins (1982)
Montreal, CAN		0.06		0.06	0.09	0.10	0.19	0.50		0.12	0.10	0.06	0.04	0.03	0.37	0.87	Env/Can (1984)
Toronto, CAN		52.90		97.39	347.11	197.32	85.61	780.33		351.52	220.24	351.88	235.41	25.16	1154.20	1934.54	Ozvacic (1984)
Quebec, CAN		4.06		14.65	15.46	12.23	1.70	48.10		45.87	35.55	38.97	8.38	0.64	129.41	177.51	Env/Can (1984)
Philidelphia NW, PA		155.00	5.43	438.33	790.00	278.33	112.83	1774.50		387.00	468.67	778.33	213.50	16.67	1864.17	3638.67	Neulict (1985)
Average of Mass Burn Facilities								653.57							1332.36	1985.94	
Refuse Derived Fuel Facilities																	
Swaru, CAN		617.50		500.00	557.50	242.50	186.25	2183.75		2560.77	2261.54	1063.08	193.85	53.85	6133.08	8316.83	Can/MOE (1984
Albany, NY		15.73	0.41	132.61	112.65	103.12	8.65	372.76		37.13	30.37	6.53	1.06	0.00	75.10	447.86	NYS/DEC (1985)
OCC. Chem, NY		93.84	2.86	99.28	224.00	225.50	115.00	757.62		199.80	339.00	168.00	67.65	13.53	787.98	1545.60	NYS/DEC (1985)
USA, (WPAFB)		30.00	9.60					30.00		312.00					312.00	342.00	Higgins (1982)
Average of Refuse Derived Fuel Facilities								836.03							1827.04	2663.07	
Controlled Air Facilities																	
PEI, CAN		3.55		10	17.23	27.08	41.9	99.75		18.1	30.6	37.63	30.45	6.23	123	222.75	Env/Can(1985)
Lake Cowichan, CAN		4.24		47.6	100.23	46.16	1.39	199.62		35.6	73.06	252.81	41.64	1.07	404.17	603.79	Env/Can (1982)
USA (N.Little Rock)		4.75	1.9					4.75		7					7	11.75	Higgins (1982)
Average of Controlled Air Facilities								101.37							178.06	279.43	

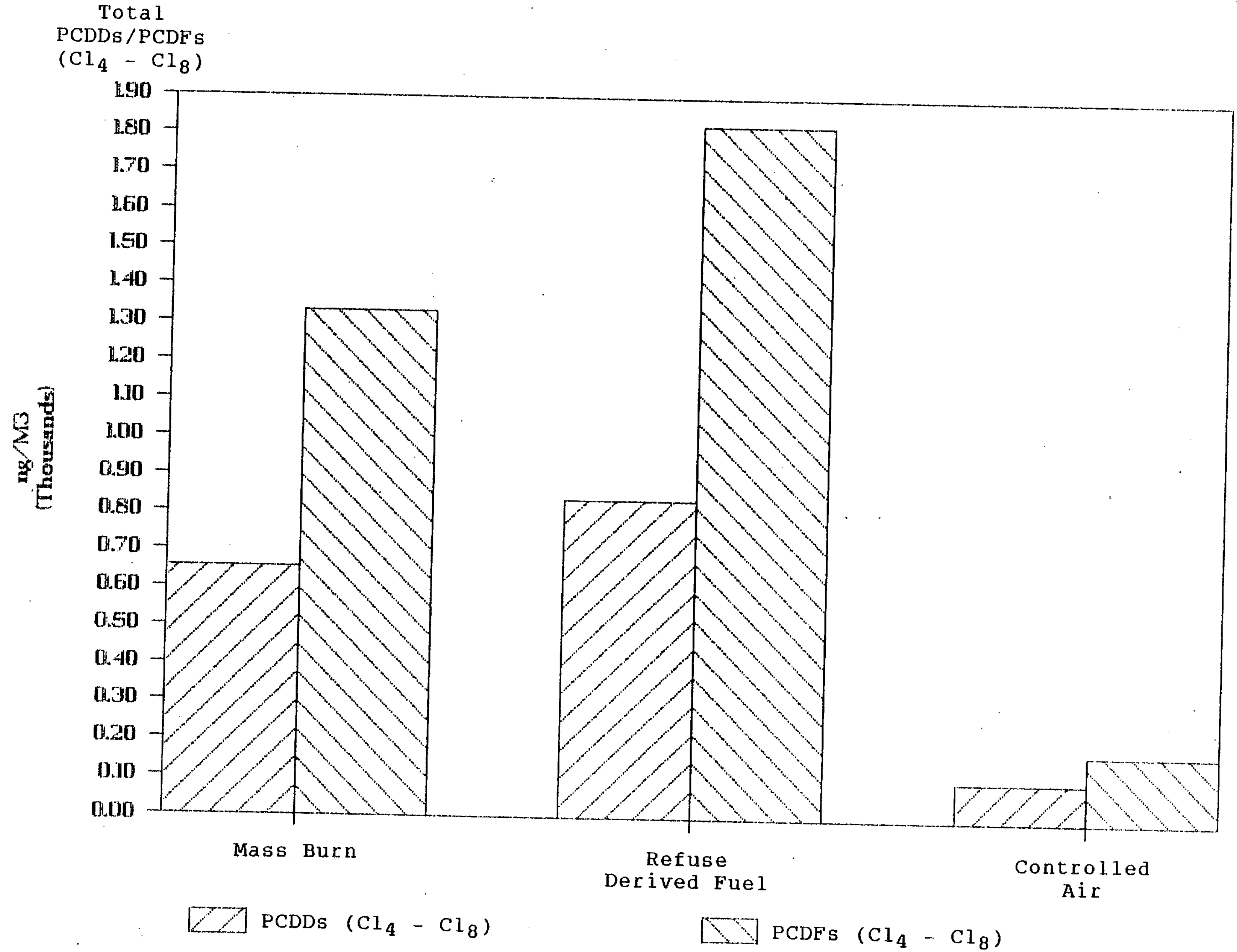

Figure 2-1 North American Resource Recovery Facilities PCDDs/PCDFs Emissions Data Summary

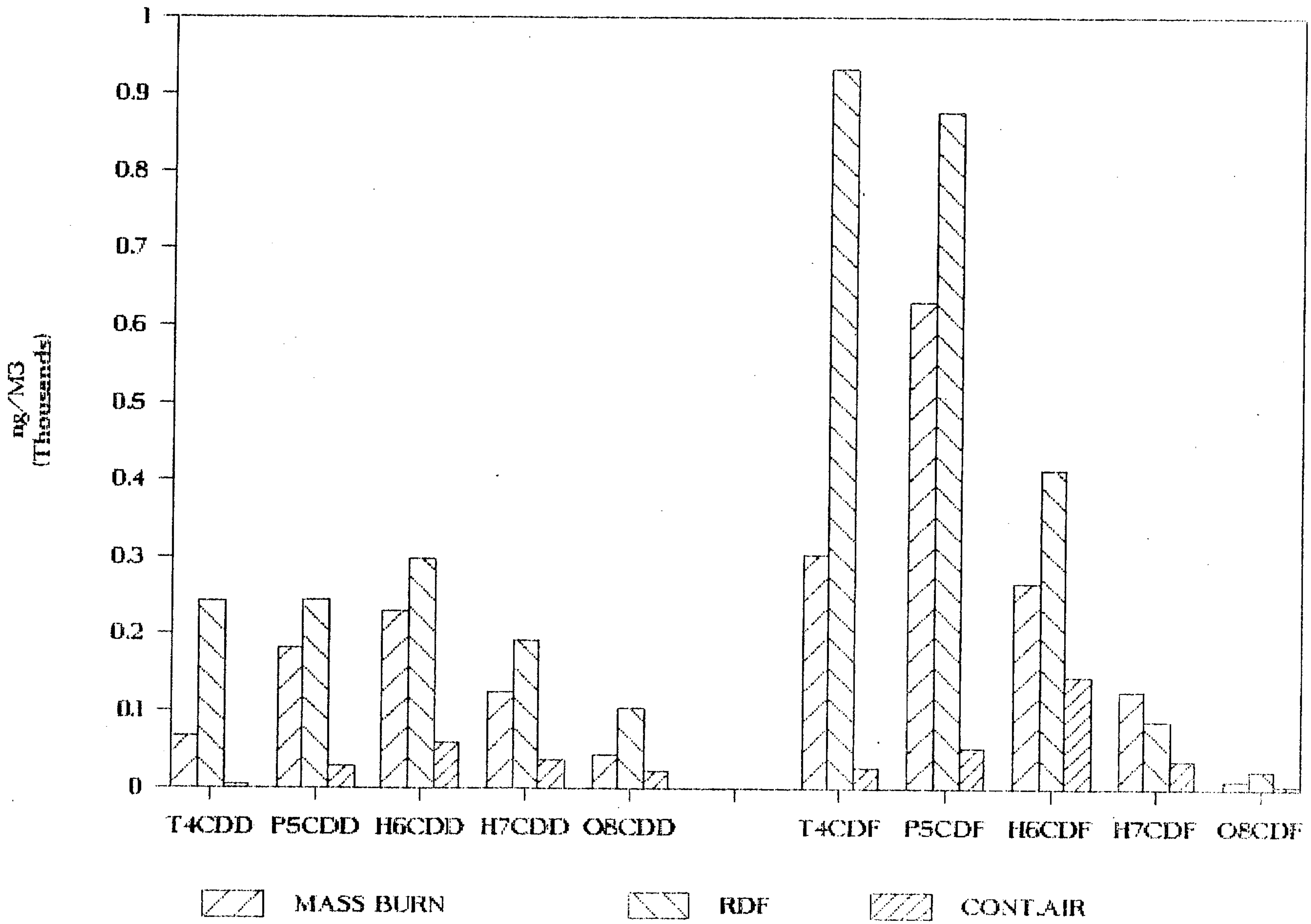

Figure 2-2 North American Resource Recovery Facilities PCDDs/PCDFs Emissions/Congener Distribution

While not specifically addressed as a discrete source category in the context of the CARB background document[1], sewage sludge incinerators are suspected of providing significant contributions of PCDDs/PCDFs to the ambient atmosphere. Sewage sludge incinerators, in fact, have been identified as a candidate source category within the aforementioned National Dioxin Strategy. Particular interest has been focused by EPA on sewage sludge incinerators which have been classified as a Rank A** source category, judged to have the greatest potential to emit TCDD.

These concerns are further heightened by specific operating practices believed to be characteristics of sewage treatment systems. These include but are not limited to the following operating practices and general characteristics of sewage waste feed:

- The likely presence of chlorinated aromatics (chlorinated benzenes, chlorinated phenols, PCBs), known precursors to PCDDs/PCDFs in industrial wastewaters that ultimately feed into the sewage treatment system itself.
- Sewage sludge incinerators are generally large systems that customarily operate around the clock and as such emissions are released on a 24 hour basis.
- Combustion parameters such as hearth temperature (700-800°C) more closely approximate favorable conditions for the formation of PCDDs/PCDFs as combustion-by-products.
- Wide variability in waste feed composition and incinerator operating conditions (e.g., hearth temperature) may further promote formation of unwanted combustion by-products.

** Rank A sources are defined as large sources with greater than 1 million tons of fuel and/or waste burned annually. Elevated dioxin precursor contamination is present in the feed/fuel. These sources have a high potential to emit TCDD and population exposure is expected to be high.

Additionally, preliminary estimates provided by Environment Canada in 1985 indicated that sewage sludge incinerators account for 1400-3000 grams of PCDDs and 1500-6500 grams of PCDFs released to the Canadian atmosphère[11].

Despite these concerns, the position that sewage sludge incinerators represent a significant source of PCDDs/PCDFs to the atmosphere was based on a limited data base at least prior to the completion of the Tier IV combustion source investigation. Prior to the release of the Tier IV results in September of 1986 the data base on PCDDs/PCDFs emissions from sewage sludge incinerators consisted of two disparate sets of flue gas emissions data, one Canadian facility[11,12] and one American facility[13], as well as the results of a grab sampling program conducted using fly ash from an aerobic sludge incinerator[14].

The results from the single Canadian survey were further extrapolated to provide a PCDDs/PCDFs emissions estimate on a nationwide basis in Canada. The result of the two American studies identified in the literature review conducted at the outset of the National Dioxin strategy are provided in Table 2-6. The results provided here for a single flue gas emissions program[15] of 483-1140 ng/m^3 PCDDs and 501-2248 ng/m^3 PCDFs corroborate well with the results reported earlier for the Canadian facility of 500-1100 ng/m^3 PCDDs and 500-2200 ng/m^3 PCDFs.

As a direct consequence of this limited data base in conjunction with EPA's preliminary categorization of sewage sludge incinerators as a Rank A source category, comprehensive PCDDs/PCDFs emissions monitoring programs were conducted at each of three sludge incineration facilities as part of the Tier IV Engineering Evaluation. The results of these three emissions programs were released in September 1986. The facilities selected were deemed to represent a cross section of sewage sludge incinerators nationwide. Facilities situated in three urban centers were selected. A brief description of each site is provided in Table 2-7.

TABLE 2-6

SEWAGE SLUDGE INCINERATORS - TIER IV INVESTIGATION

PCDDS/PCDFS EMISSIONS SUMMARY[15]

Type of Facility	No. of Units Tested (Location)	Sample	PCDD/PCDF Emission Concentration an Ash Sample Content					
			2378-TCDD		PCDD		PCDF	
			Mean	Range	Mean	Range	Mean	Range
Multiple Hearth	1	FG	-	-	739 ng/m^3	483-1,140 ng/m^3	1,213 ng/m^3	501-2,248 ng/m^3
Unspecified	1	Fumes[a]	-	-	ND[b]	-	-	-
		Ashes[a]	-	-	ND[b]	-	-	-

[a]Matrices are listed as reported in document
[b]Not detected

TABLE 2-7

SEWAGE SLUDGE INCINERATORS

SUMMARY DESCRIPTION OF TIER IV SITES

Site	Description
A	3.75 wet Envirotech six-hearth incinerator controlled by a cyclone followed by a venturi/impingement tray scrubber. Average industrial constribution to treatment plant influent.
B	12.5 wet TPH Envirotech nine-hearth incinerator controlled by a cyclone followed by a waste heat boiler, a venturi scrubber and a subcooler. Average industrial contribution to treatment plant influenet. Installed in 1983. Owned and operated by the Metropolitan Wastewater Commission (MWCC). Services the Minneapolis/St. Paul Minnesota metropolitan area.
C	13.5 wet TPH Nichols twelve-hearth multiple hearth incinerator controlled by a 3 tray impingement scrubber. High industrial contribution to treatment plant influent. Installed 1974. Services the Detroit, Michigan Metropolitan area.

Per specifications in the National Dioxin Strategy, each source was monitored for each of the Cl_4-Cl_8 PCDDs/PCDFs congener classes as well as the 2,3,7,8-TCDD/TCDF isomers. Each emissions characterization program consisted of a series of three tests conducted while the respective incinerator was maintained under "steady state" or representative operating conditions.

Emissions data for the three facilities consisting of average values of the "candidate" PCDDs/PCDFs collected during each of three test series are plotted graphically in Figure 2-3. The results provided here further support the wide variability in PCDDs/PCDFs emissions that can be expected when comparing data from several facilities within a source category. More specifically, the results provided in SSI-C (Detroit, Michigan) more closely approximate the existing data base while the data provided for facilities SSI-A and SSI-B seem to indicate that PCDDs/PCDFs emissions from this source category may not be that significant. In a manner consistent with emissions data from other source categories, PCDFs emissions seem to predominate over the PCDDs congeners. These findings are further corroborated as a result of a second emissions monitoring program conducted at the MWCC facility (Minneapolis/St. Paul) in May of 1986 by ERT[16]. A comparison of these data to the aforementioned Tier IV data is provided in Figure 2-4. As the PCDFs congeners again predominate over the PCDDs. Furthermore, the PCDFs emissions are predominated by the TCDF (Cl_4) congener category and to a lesser extent the Cl_5 and Cl_6 PCDFs congener classes. Refer to Figure 2-5 for a direct comparison of the ERT 1986 test program to 1985 tier IV by PCDFs congener category[17].

In addition to the remarkable agreement in comparing results for the two emissions programs, the data sets indicate further that the TCDFs (Cl_4) congener class predominates, comprising between 65-70% of the combined PCDDs/PCDFs (Cl_4 - Cl_8) emissions from sewage sludge incinerators as shown in Figure 2-6.

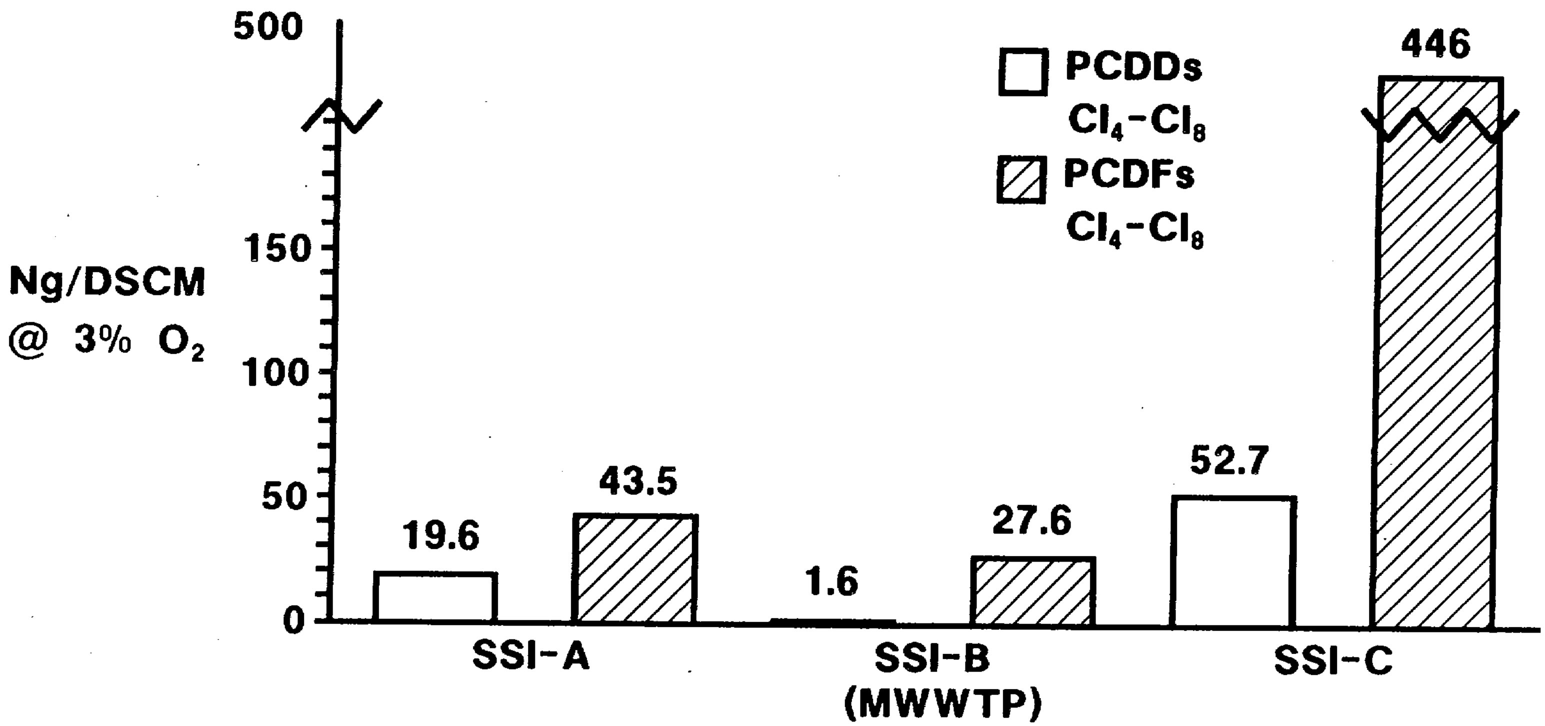

Figure 2-3 Tier IV Sewage Sludge Incinerators (SSI) PCDDs/PCDFs Emissions Data Summary

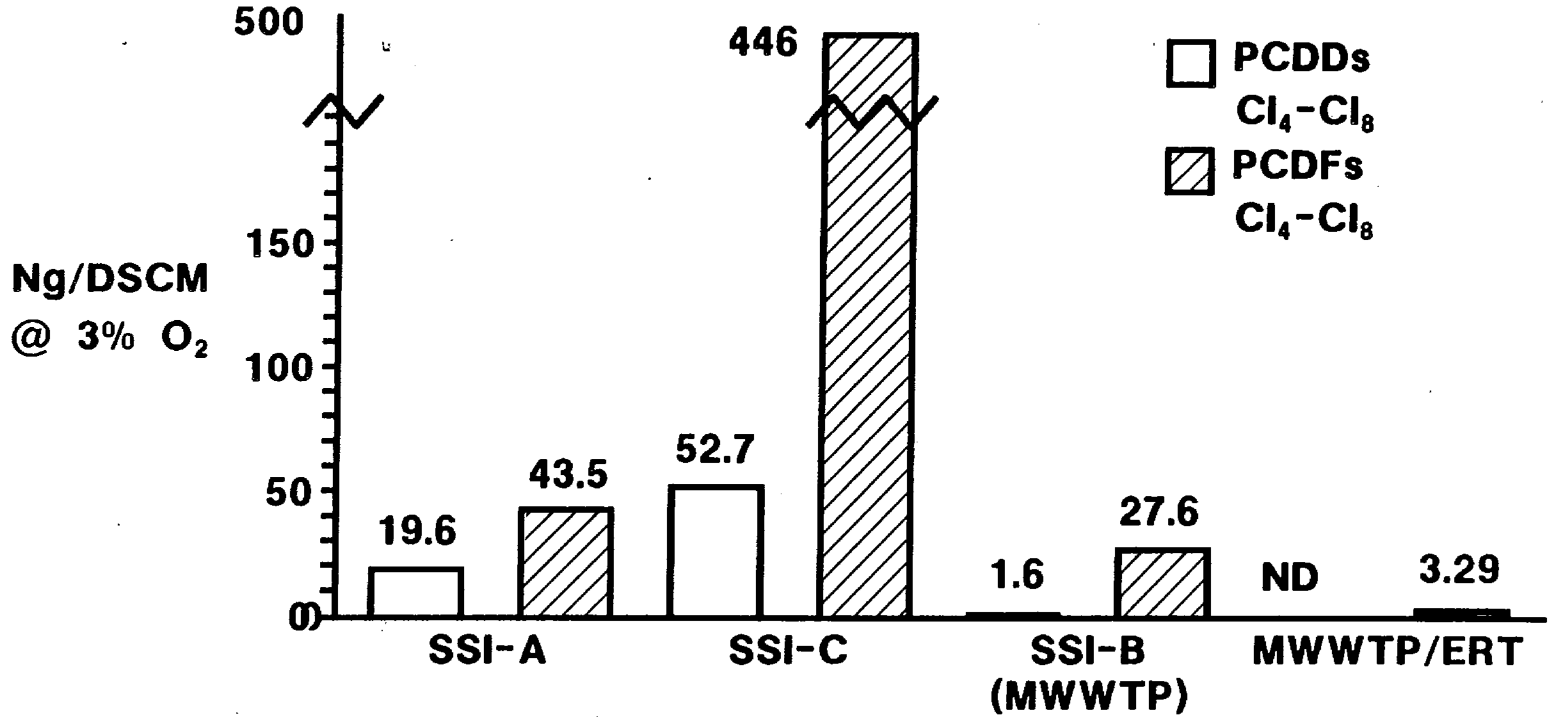

Figure 2-4 Comparison of PCDDs/PCDFs Emissions Data - MWWTP (ERT) and Tier IV

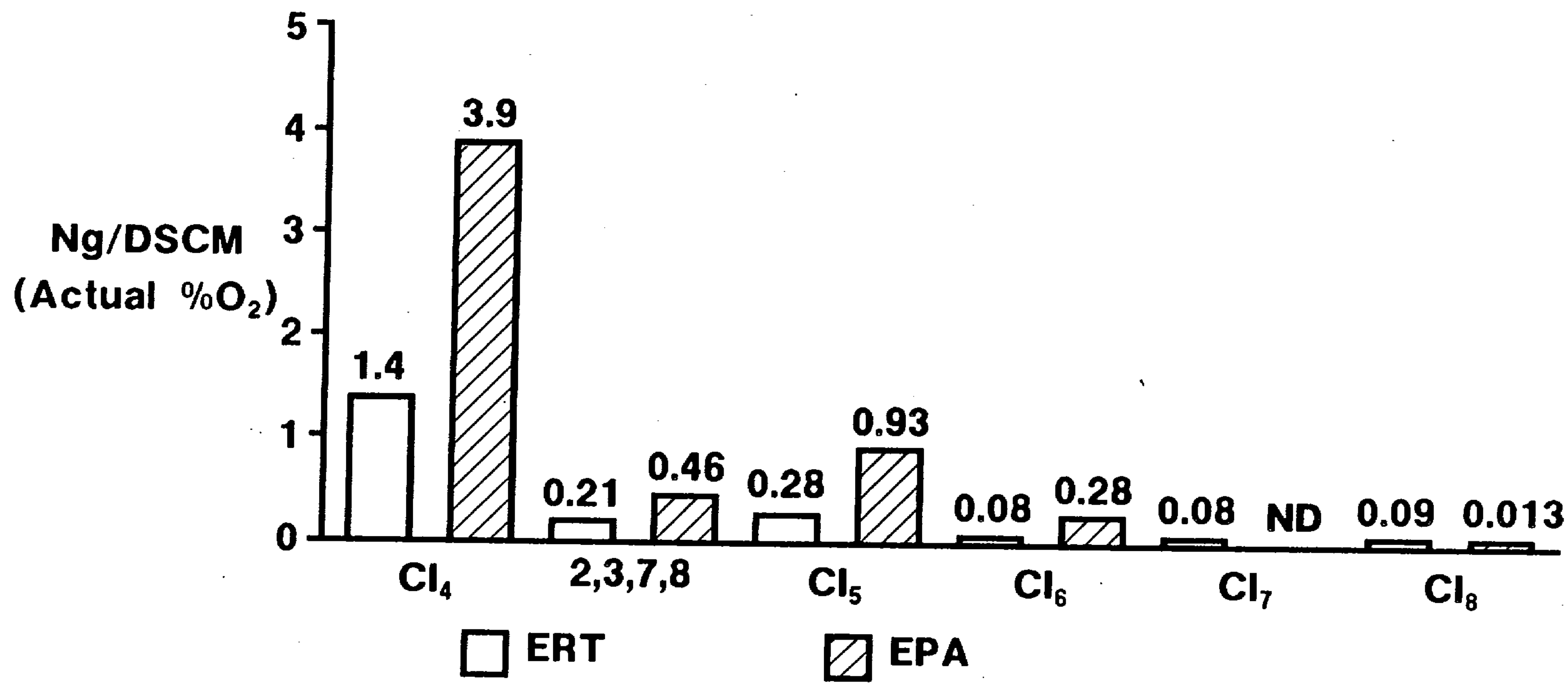

Figure 2-5 PCDFs Emissions MWWTP (Cl_4 - Cl_8) Comparison of Data - ERT and EPA

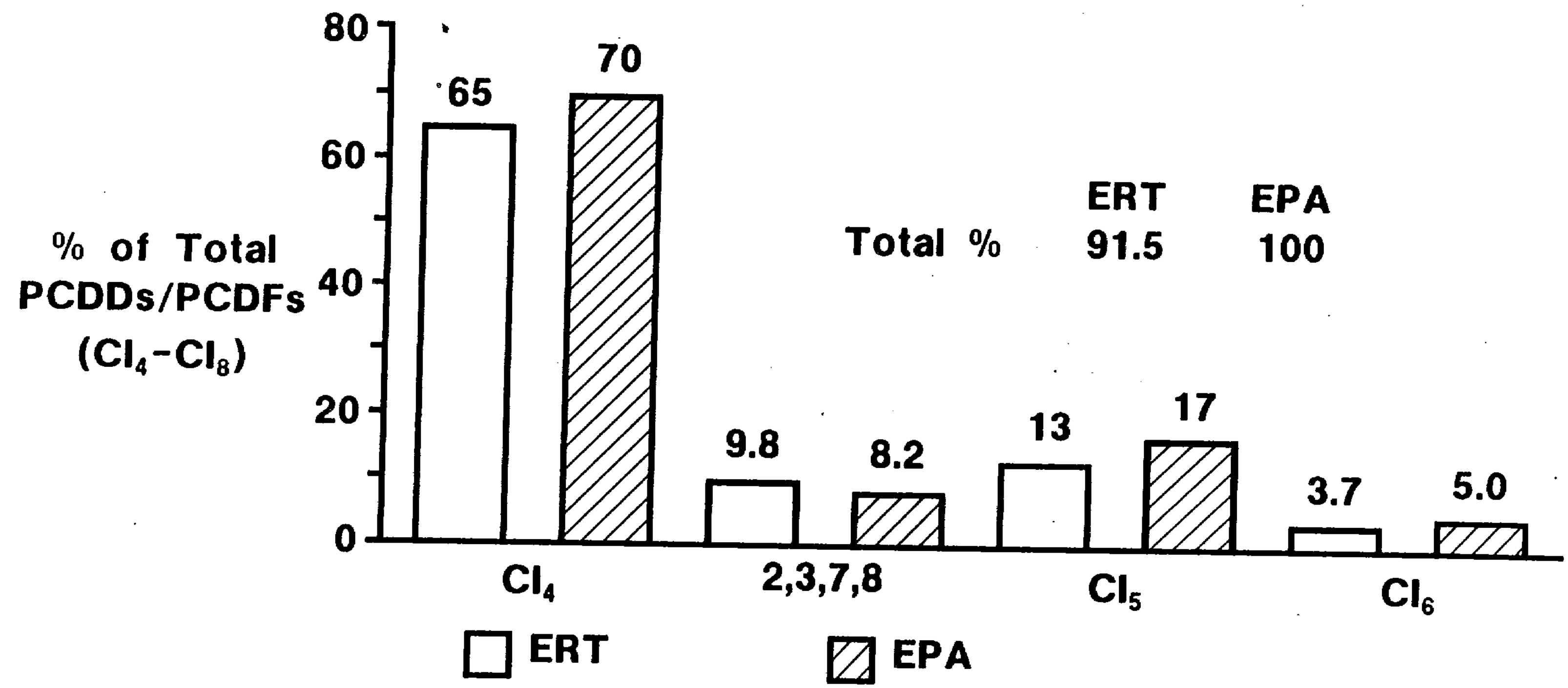

Figure 2-6 PCDFs Emissions MWWTP (Cl_4 - Cl_6) % Composition Data - ERT and EPA

The toxicologically significant 2,3,7,8 TCDF isomer represents but a small portion of this total. These findings certainly have particular implications when assessing sewage sludge incinerators as a significant source of TCDDs/TCDFs or even PCDDs/PCDFs for that matter.

2.3.3 Hospital Waste Incinerators

The composition of hospital wastes, including chlorinated disinfectants, drugs and pathological wastes, presents the potential for formation of PCDDs and PCDFs. High temperature incineration is the preferred method for disposal of these wastes. Most hospital incinerators of older design are incapable of destroying all hazardous materials and have inefficient combustion leading to emission of hazardous air pollutants. Hospital wastes are also highly variable in content and contain approximately 20-30% plastics, compared to municipal solid waste with 3-7% plastics. Since plastics are typically polyvinyl chloride (PVC) or other halogenated polymers, combustion of wastes with high plastics content can be a major source of toxic air emissions, including PCDD's and PCDF's.

Although many hospitals have their own incineration systems, actual test results for PCDD's and PCDF's are fairly limited. Table 2-8 summarizes the results of incinerator testing found in the open literature. Doyle _et al_[18] reported results from three hospital incinerators tested in the United States. Stack test filter samples were analyzed and had average levels of PCDD's and PCDF's of 15 ng/m3 and 25 ng/m3, respectively. These levels probably represent less than half of the actual emissions since the levels of PCDD's and PCDF's present in the vapor phase were not determined.

Information is also available on tests performed at a Canadian hospital incinerator[19] and on two incinerators located in California[20,21]. The results are shown in Table 2-8 and Figure 2-7.

TABLE 2-8

HOSPITAL INCINERATION TEST RESULTS

Facility		PCDD EMISSIONS (ng/M3)								PCDF EMISSIONS (ng/M3)								
		T3CDD	T4CDD	2,3,7,8 T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	TOTAL CDD	T3CDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	TOTAL CDF	TOTAL PCDD + PCDF	REFERENCE
Canada Royal Jubilee Victoria, B.C.			ND		15.7	13.8	16.7	22.8	68.9		27.0	46.2	42.9	25.7	13.8	155.6	224.5	Bumbaco 1983
St.Agnes Med Ctr Fresno, CA	Run 1		38.5		23.5	54.4	137.0	196.0	450.0		64.9	136.0	202.0	232.0	150.0	785.0		
	Run 2		3.3		18.2	38.7	85.5	145.0	290.0		78.7	130.0	170.0	160.0	166.0	704.0		
	Average		20.9		20.9	46.6	111.3	170.5	370.0		71.8	133.0	186.0	196.0	158.0	744.5	1114.5	CARB 1987a
Cedars-Siani Med Ctr Los Angeles, CA				0.3	1.4	6.1	23.2	32.8	63.8		1.9	13.4	35.2	69.4	43.5	163.4	227.2	CARB 1987b
Doyle #1									11.8							18.9		EPA 450/4-84-014h
Doyle #2									28.2							52.1		
Doyle #3									4.8							4.8		
	Average								14.9							25.3		

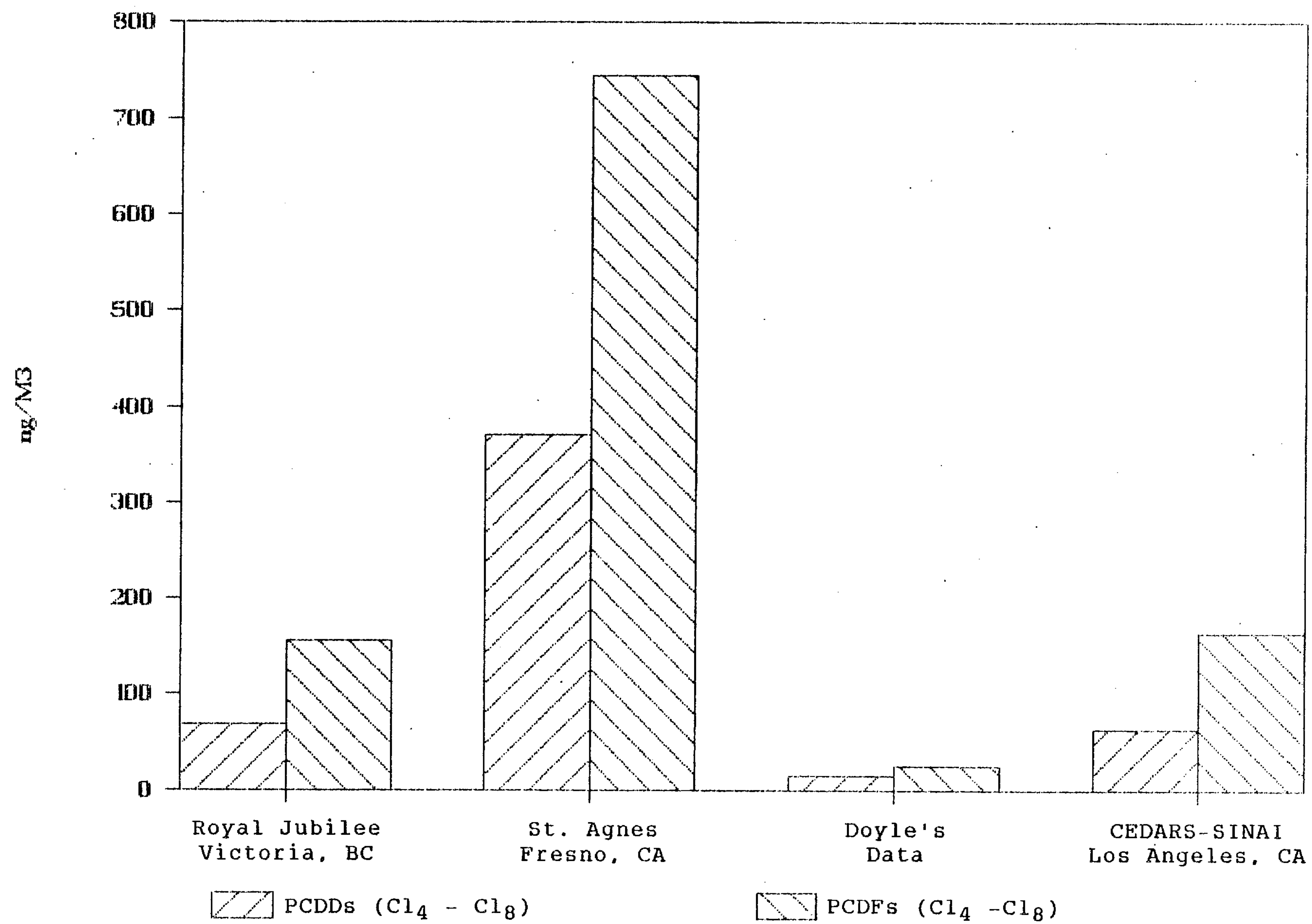

Figure 2-7 Hospital Incinerators PCDDs/PCDFs Emissions Data Summary

Test data reported for the Canadian and the two California hospital incinerators was broken down by congener. The distribution, shown on Figure 2-8, demonstrates that for both dioxins and furans, the hexa-, hepta- and octa-congeners predominate; compared to resource recovery facilities (Figure 2-2) and sewage sludge incinerators (Figure 2-5) in which the tetra- and penta-homologues are most common.

The hospital waste incinerators currently operating in the South Coast Air Basin are summarized in Table 2-9. This listing was obtained from the SCAQMD[22] and consists of all sources in the basin with category codes beginning with 00013, 00014, 00015 and 00018. (The complete SCAQMD listing can be found in Appendix I.) Some of the sources in these specific categories, however, were excluded from Table 2-9 since they were clearly either incinerators handling strictly pathological waste or crematoriums. Such facilities are not expected to be sources PCDDs or PCDFs since the wastes they handle do not contain plastics and other materials (e.g. chlorinated aromatics) commonly identified as precursors to PCDDS/PCDFS.

Hospital waste incinerators were assigned Rank C in the recently completed National Dioxin Tier 4 study[15]. Further stack testing of these sources was not performed as part of the Tier IV program since the high combustion temperatures used indicated a low potential for PCDDs and PCDFs formation.

2.3.4 Wire Reclamation Incinerators

Incineration is a commonly used method for the recovery of metals from wire scrap. The combustible portion of wire insulation can be comprised of a wide variety of materials, including rubber, paper, cotton, and a large variety of plastics. Thermal degradation of insulation materials can lead to emissions of PCDD's and PCDF's.

Emissions data from wire reclamation units was limited prior to the Tier 4 study[10]. One test result on ash samples was available in the open literature[23]. Stack residue PCDD and PCDF concentrations were reported to be 0.41 ng/g and 11.6 ng/g, respectively.

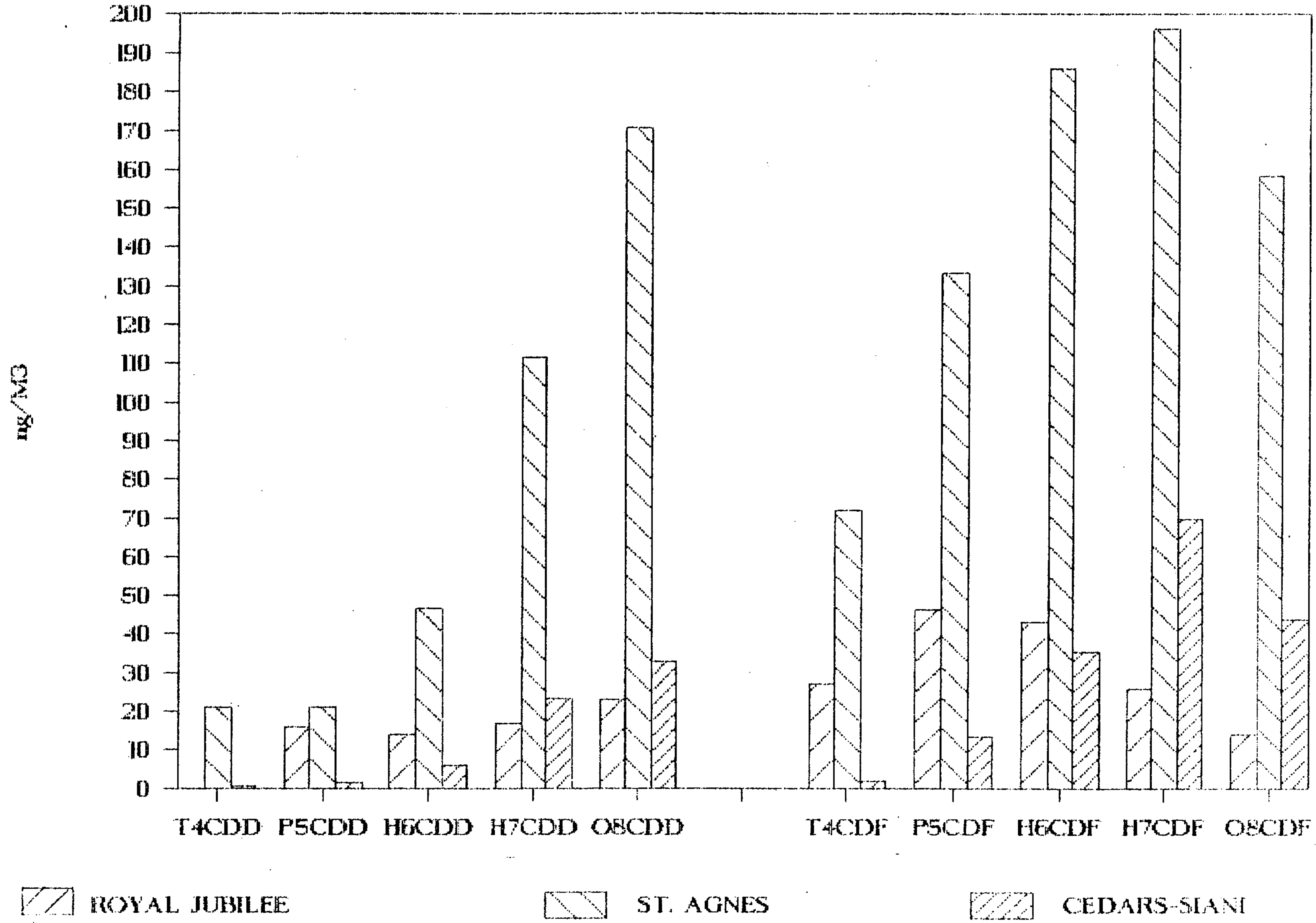

Figure 2-8 Hospital Emissions Congener Distribution

TABLE 2-9

LISTING OF HOSPITAL INCINERATORS IN THE SOUTH COAST AIR BASIN

CITY	COMPANY NAME	ADDRESS
ANAHEIM	PARKVIEW HOSPITAL	1514 EAST LINCOLN AVENUE
BANNING	SAN GORGONIO PASS MEMORIAL HOSP.	600 N. HIGHLAND SPRINGS AV.
BELLFLOWER	L.A. CO., BELLFLOWER HEALTH CTR.	10005 E. FLOWER STREET
BIG BEAR LAKE	BEAR VALLEY COMM. HOSP. DIST.	41870 GARSTIN DRIVE
BURBANK	BURBANK COMMUNITY HOSPITAL	466 EAST OLIVE AVENUE
BURBANK	ST. JOSEPHS HOSP. AND MEDICAL CTR.	501 S. BUENA VISTA AVENUE
CARSON	STAUFFER CHEMICAL CO. UNIT #2	20720 S. WILMINGTON AVENUE
DOMINGUEZ HILLS	CAL. STATE COL., DOMINGUEZ HILLS	1000 EAST VICTORIA STREET
DUARTE	CITY OF HOPE MEDICAL CENTER	1500 DUARTE ROAD
DUARTE	CITY OF HOPE MEDICAL CENTER	2104 BUENA VISTA STREET
EL MONTE	L.A. CO., EL MONTE HEALTH CENTER	3550 EASTMONT
FONTANA	KAISER FONTANA HOSPITAL	9961 SIERRA AVENUE
FULLERTON	CAL. STATE UNIV., FULLERTON	800 N. STATE COLLEGE BLVD.
FULLERTON	ST. JUDES HOSPITAL AND REHAB. CTR.	101 S. VALENCIA MESA DRIVE
GLENDALE	GLENDALE ADVENTIST MEDICAL CTR.	1509 WILSON TERRACE
GLENDALE	GLENDALE MEM. HOSP. & HEALTH CTR.	1420 S. CENTRAL AVENUE
GLENDALE	L.A. CO., GLENDALE HEALTH CENTER	501 NORTH GLENDALE AVE.
HEMET	CLOVERLEAF HEALTH CARE	275 N. SAN JACINTO STREET
HEMET	HEMET CONVALESCENT HOSPITAL	40300 DEVONSHIRE AVENUE
HEMET	MEADOWBROOK CONVALESCENT HOSP.	461 EAST JOHNSTON STREET
INDIO	JONH F. KENNEDY MEMORIAL HOSPITAL	47 - 111 MONROE STREET
INGLEWOOD	INGLEWOOD ANIMAL HOSPITAL INC.	817 W. MANCHESTER BLVD.
LA PUENTE	L.A. CO., LA PUENTE HEALTH CENTER	15930 CENTRAL AVE.
LAKEWOOD	DOCTOR'S HOSP. OF LAKEWOOD	3700 EAST SOUTH STREET
LOMA LINDA	LINDA VALLEY CONVALESCENT HOSP.	25383 COLE STREET
LOMA LINDA	LOMA LINDA COMMUNITY HOSPITAL	25333 BARTON ROAD
LOMA LINDA	U.S. GOVT., VETERANS ADMIM. HOSP.	11201 BENTON STREET
LOS ANGELES	BARLOW HOSPITAL	2000 STADIUM WAY
LOS ANGELES	BROADVIEW SANITORIUM	4570 GRIFFIN AVE.
LOS ANGELES	CAL. STATE UNIVERSITY, L.A.	5151 STATE UNIVERSITY DR.
LOS ANGELES	CALIF. MEDICAL CTR. - L.A.	1414 SOUTH HOPE STREET
LOS ANGELES	CEDARS-SINAI MEDICAL CENTER	6700 ALDEN DRIVE
LOS ANGELES	CHILDREN'S HOSPITAL OF L.A.	4614 SUNSET BOULEVARD
LOS ANGELES	CIGNA	1711 TEMPLE STREET
LOS ANGELES	GATEWAYS HOSPITAL	1891 EFFIE STREET
LOS ANGELES	HOLLYWOOD PRESBYTERIAN MED. CTR.	1300 NORTH VERMONT AVE.
LOS ANGELES	KEIRO NURSING HOME INC.	2221 LINCOLN PARK AVE.
LOS ANGELES	L.A. CITY CENTRAL MEDICAL CENTER	1401 SIXTH STREET
LOS ANGELES	L.A. CO SYBIL BRAND INST FOR WOMEN	4500 E. CITY TERRACE DRIVE
LOS ANGELES	L.A. CO., ADM HDQRS, HEALTH DEPT	313 N. FIGUEROA STREET
LOS ANGELES	L.A. CO., SO. DISTRICT HEALTH CTR.	1522 EAST 102TH STREET
LOS ANGELES	L.A. CO., UNIV. S. CAL. MED. CTR.	1200 NORTH STATE STREET
LOS ANGELES	LOYOLA MARYMOUNT UNIVERSITY	7101 WEST 80TH STREET
LOS ANGELES	SOLHEIM LUTHERAN HOME	2236 MERTON AVENUE
LOS ANGELES	TEMPLE HOSPITAL	235 NORTH HOOVER STREET
LOS ANGELES	U.S. GOVT., VETERANS ADMIM. HOSP.	WILSHIRE AND SAWTELLE
LOS ANGELES	UNIV. SO. CAL. PHYSICAL PLANT DEPT	2011 ZONAL AVENUE
LOS ANGELES	UNIV. SO. CAL. PHYSICAL PLANT DEPT	UNIVERSITY PARK
LOS ANGELES	UNIVERSITY OF CALIFORNIA L.A.	405 HILGARD AVENUE

TABLE 2-9 (Continued)

MARCH AFB	U.S. GOVT., MARCH AFB, UNIT #1	EAST OF HIGHWAY 395
MONTEBELLO	BEVERLY HOSPITAL	309 N. BEVERLY BLVD.
MONTEREY PARK	GARFIELD MEDICAL CENTER	525 NORTH GARFIELD AVENUE
MURRIETA	INTERNATIONAL IMUNOLOGY CORP.	22549 ADAMS AVENUE
NORTHRIDGE	CAL. STATE UNIV., NORTHRIDGE	18111 NORDHOFF STREET
ORANGE	UNIVERSITY CALIF. IRVINE MED. CTR.	101 CITY DRIVE SOUTH
PALM SPRINGS	CAL. NURSING & REHAB. CTR.	2299 NORTH INDIAN AVENUE
PASADENA	HUNTINGTON MEMORIAL HOSPITAL	100 NORTH CONGRESS STREET
PERRIS	CHRISTIAN HOSPITAL MEDICAL CTR.	2224 RUDY DRIVE
POMONA	CAL. ST. - F D LANTERMAN ST. HOSP.	3530 WEST POMONA BLVD.
POMONA	CAL. STATE POLYTECH. UNIVERSITY	3801 WEST TEMPLE AVE.
POMONA	CASA COLIMA HOSP. FOR REHAB. MED.	255 EAST BONITA AVE.
POMONA	L.A. CO., POMONA HEALTH CENTER	750 SOUTH PARK
RIALTO	CRESTVIEW CONVALESCENT HOSPITAL	1471 RIVERSIDE
RIVERSIDE	ALTA VISTA CONVALESCENT HOSP.	9020 GARFIELD
RIVERSIDE	BEVERLY MANOR CONVALESCENT HOSP.	4768 PALM AVENUE
RIVERSIDE	COMMUNITY CONVALESCENT HOSPITAL	4070 JUROPA AVENUE
RIVERSIDE	EXTENDED CARE HOSP. OF RIVERSIDE	8171 MAGNOLIA AVENUE
RIVERSIDE	MT. RUBIDOUX REHABILITATION HOSP.	6401 33RD STREET
RIVERSIDE	PARKVIEW COMMUNITY HOSPITAL	3865 JACKSON STREET
RIVERSIDE	RIVERSIDE COMMUNITY HOSPITAL	4445 MAGNOLIA AVENUE
RIVERSIDE	UNIVERSITY OF CALIF. RIVERSIDE	STEAM PLANT-UCR
SAN BERNARDINO	CAL. STATE UNIV., SAN BERNARDINO	5500 STATE UNIV. PARKWAY
SAN BERNARDINO	SAN BERNARDINO CO. MEDICAL CENTER	780 EAST GILBERT
SAN BERNARDINO	ST. BERNARDINE HOSPITAL	2101 NORTH WATERMAN AVE.
SANTA ANA	CAREHOUSE CONVALESCENT HOME	1800 N. OLD TUSTIN AVE.
SANTA MONICA	SANTA MONICA HOSPITAL MEDICAL CTR.	1225 15TH STREET
SEPULVEDA	U.S. GOVT., VETERANS ADMIM. HOSP.	16111 PLUMMER STREET
SOUTH LAGUNA	SOUTH COAST MEDICAL CENTER	31872 COAST HIGHWAY
STUDIO CITY	H.G. TULLY VETERINARY HOSPITAL	11966 VENTURA BOULEVARD
SUN CITY	SUN CITY REHABILITATION CENTER	27600 ENCANTO DRIVE
SYLMAR	L.A. COUNTY, OLIVE VIEW MED. CTR.	14445 OLIVE VIEW DRIVE
TORRANCE	L.A. CO., TORRANCE HEALTH CENTER	2300 WEST CARSON STREET
TORRANCE	L.A. COUNTY, HARBOR GENERAL HOSP.	1000 WEST CARSON STREET
TORRANCE	SIDNEY JARED TORRANCE MEM. HOSP.	3330 LOMITA BOULEVARD
UPLAND	SAN ANTONIO COMMUNITY HOSPITAL	999 SAN BERNARDINO
VAN NUYS	VALLEY HOSP. MED. CTR./HEALTH WEST	14500 SHERMAN CIRCLE
YORBA LINDA	ST. JUDES HOSPITAL, YORBA LINDA	16850 GASTANCHURY ROAD

Due to this lack of test data, these sources were classified as Rank B during the Tier 4 study. One facility was chosen for testing; it was considered to be a "high" potential site because the feed contained some PVC coated wire and PCB-contaminated transformer cores. In addition, small (<200 ppb) quantities of chlorophenols were found in both feed materials. The result of this test is shown in Table 2-10.

A listing of wire reclamation incinerators operating in the South Coast Air Basin was obtained from SCAQMD (Source Category 000190) and is shown in Table 2-11.

2.4 Area Sources as Potential Sources of PCDDs/PCDFs

In addition to the stationary combustion sources identified in Section 2.3 as potential sources of chlorinated dioxins and furans, several area source categories were identified which should also be considered as potential dioxin/furan sources. Fugitive emissions from these sources may contribute to ambient levels of PCDDs/PCDFs in the area of these sources and should therefore be examined. Table 2-12 lists potential area sources of PCDDs/PCDFs as identified by EPA and the California Air Resources Board (CARB).[2,24] Area source categories represented in the South Coast Air Basin and under consideration for the present program include hazardous waste sites, wood treatment facilities, and aggregated mobile sources, such as automobiles. These categories are discussed in the following sections in terms of their role as potential sources of PCDDs/PCDFs.

2.4.1 Hazardous Waste Sites

Hazardous waste sites serve as potential sources of PCDDs/PCDFs as a result of direct contamination with dioxin/furan containing waste or known dioxin/furan precursors. These precursors are thought to include chlorinated compounds such as polychlorinated biphenyls (PCBs),

TABLE 2-10

SUMMARY OF WIRE RECLAMATION INCINERATOR DATA

	PCDD EMISSIONS (ng/M3)								PCDF EMISSIONS (ng/M3)								
Facility	T3CDD	T4CDD	2,3,7,8 T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	TOTAL CDD	T3CDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	TOTAL CDF	TOTAL PCDD + PCDF	REFERENCE
WRI-A (wire and transformer feed)			0.1					705.0							866.0	1571.0	EPA 450/4-84-014h
WRI-A (wire only feed)			0.1					173.0							305.0	478.0	EPA 450/4-84-014h

TABLE 2-11

LISTING OF WIRE RECLAMATION INCINERATORS IN THE SOUTH COAST AIR BASIN

CITY	COMPANY NAME	ADDRESS
ALHAMBRA	COMMERCIAL ELECTRIC MOTORS INC.	1101 MERIDIAN AVENUE
CARSON	STATE SALVAGE COMPANY INC.	22500 SOUTH ALAMEDA STREET
CORONA	CORONA ELECTRIC MOTORS	1781 CAPITAL ST., UNIT 1
CORONA	SIX-PAC RECYCLING CENTER	14292 EAST 6TH STREET
FONTANA	FRANKEL IRON AND METAL COMPANY	15615 ARROW HIGHWAY
HEMET	HEMET ELECTRIC MOTOR SERVICE	141 SOUTH INEZ STREET
INDIO	DESERT MOTOR REWIND	84191 INDIO BOULEVARD
LOS ANGELES	PAN METAL CORPORATION	720 EAST 59TH STREET
LOS ANGELES	STUMP ELECTRIC COMPANY INC.	3414 EAST 14TH STREET
PICO RIVERA	ROSEN'S ELECTRICAL EQUIP. CO. INC.	8226 EAST WHITTIER BLVD.
S. EL MONTE	COMPRESSOR PARTS & REPAIR INC.	1501 NORTH PECK ROAD
VERNON	LITTLEJOHN-REULAND CORPORATION	4575 PACIFIC BOULEVARD
WALNUT	EMERSON ELECT. CO., IND. SERV DIV.	19888 QUIROZ CT.

TABLE 2-12

AREA SOURCE CATEGORIES IDENTIFIED BY EPA AND THE CALIFORNIA AIR RESOURCES BOARD AS POTENTIAL SOURCES OF PCDDs/PCDFs

Potential PCDD/PCDF Area Source Categories Identified by EPA

- 2,4,5-trichlorophenol (245-TCP) production sites and associated waste disposal sites
- sites where 2,4,5-TCP was used as a precursor to make pesticidal products
- sites where 2,4,5-TCP and its derivatives were formulated into pesticidal products
- sites where pesticides derived from 2,4,5-TCP have been and are being used on a commercial basis

Potential PCDD/PCDF Area Source Categories Identified by the California Air Resource Board

- mobile sources (e.g., automobiles)
- wood stoves/fireplaces
- forest fire/agricultural burning

pesticides, chlorinated benzenes and other chlorinated hydrocarbons. Table 2-13 lists the hazardous waste sites in the South Coast Air Basin which contain chlorinated wastes, and as a result, are worthy of consideration as potential sources of PCDDs/PCDFs[24]. The sites contained in this list were identified from a complete list of California hazardous waste sites published in the "Expenditure Plan for the Hazardous Substance Cleanup Bond Act of 1984--Revised 1987" by the California Department of Public Health[25].

2.4.2 Wood Treatment Facilities

Wood treatment facilities have been identified by the EPA as a potential source of PCDDs and PCDFs (see Table 2-12). The dioxin/furan emissions which may occur at these facilities are primarily a result of pentachlorophenol (PCP) used in the wood treatment process. Presently, there is one (1) operational wood treatment facility in the South Coast Air Basin, located in Long Beach, as detailed in Table 2-14. This facility utilizes a pressure-treating process which entails placing the wood in a sealed chamber for treatment. The most likely dioxin and furan emission sources resulting from this process are off-gas from the wood after treatment and release of gas upon opening the treatment chamber after wood treatment is completed.

2.5 Atmospheric Concentration of PCDDs/PCDFs

2.5.1 Overview/Introduction

As discussed previously in Sections 2.1 and 2.2, a comprehensive review of the open literature in combination with a telephone survey of the active technical community was conducted in an effort to identify existing data on the distribution and occurrence of PCDDs/PCDFs in the ambient atmosphere. It was anticipated that such data, if available, would serve the following purposes:

TABLE 2-13

HAZARDOUS WASTE SITES IN THE SOUTH COAST AIR BASIN--AREA SOURCES SERVING AS POTENTIAL SOURCES OF PCDDs/PCDFs TO THE AMBIENT ATMOSPHERE

Site Name	Site Location: Address	Site Location: City	Waste Type
Dean and Associates	700 S. Santa Fe Ave.	Los Angeles	PCBs
Del Amo Boulevard	Del Amo Blvd.	Torrance	chlorinated benzenes, benzo(b)fluoranthene, benzo(a)pyrene
Space Ordinance Systems	34854 Peterson Road	Canyon Country	MEK, 1,2,4-trichlorobenzene, trichloroethylene
Space Ordinance Systems	25977 Sand Canyon Road	Newhall	1,2,4-trichlorobenzene, trichloroethylene
Ascon Landfill	21641 Magnolia Street	Huntington Bch	1,1,1-trichloroethylene, perchloroethylene
CAL Compact Landfill	20300 S. Main Street	Carson	chlorinated pesticides, herbicides, paints, dyes
CAL Trans I-105 Freeway Project	120 Spring Street	Los Angeles	PCBs, cyanides, halogenated organics
Commerce Refuse to Energy Authority	5900 Sheila Street	Commerce	chlorinated solvents, acetone
Continental Moulding Facility	Taft Avenue	Orange	pentachlorophenol contaminated sludge
Edington Oil Company	2400 E. Artesia Blvd.	Long Beach	chlorinated hydrocarbons, vinyl chloride, TCE
Facet Energy	3020 Orange Ave.	Long Beach	organic solvents, halogenated organic compounds
GATX Annex Terminal	GATX Annex Terminal	San Pedro	chlorinated solvents
Hughes Helicopters, Inc.	Centinela Ave.	Culver City	TCE, vinyl chloride, dichloroethane, dichloroethylene
Koppers, Los Angeles	210 S. Avalon Blvd.	Wilmington	pentachlorophenol
Stauffer Chemical	3250-3294 E. 26th St.	Vernon	contaminants unknown
TCL Corporation	420 Henry Ford Ave.	Wilmington	PCBs, solvents, dyes
University of California, Riverside	1060 Pennsylvania Ave	Riverside	phosgene, chlorinated hydrocarbon pesticides and solvents
VOI-SHAN Redondo Beach	4001 Inglewood Ave.	Redondo Beach	1,1,1-trichloroethane, 1,1-dichloroethylene
Neville Chemical Company	12800 E. Imperial	Santa Fe Spr.	Dichlorobenzenes, dibenzofurans
Orange County Steel Salvage	3200 Frontera Rd.	Anaheim	PCBs
Southland Oil, Inc.	5619-5621 Randolph St.	Commerce	chloroform, PCBs, benzene
Montrose Chemical	20201 Normandie Ave.	Torrance	DDT
San Fernando Valley	San Fernando Valley	S.F. Valley	perchloroethylene, TCE
Air Force Plant 42	Palmdale Airport	Palmdale	PCBs, solvents, paint, heavy metals
Dagget Airport	Dagget Airport	Dagget	pesticides, explosives, solvents, fuels suspected
El Toro Marine Corps Air Station	Marine Corps Air St.	El Toro	pesticides, PCBs, radium isotopes
George Air Force Base	George AFB	Victorville	pesticides, PCBs, cleaning solvents, paint
Endura Metals	6900 Stanford Ave.	Los Angeles	extensive PCB contamination
Leeder Chemicals Company	16961 Knott Ave.	La Mirada	1,1,1-trichloroethane
Twentynine Palms Marine Center	Twentynine Palms M.C.	Twentynine Pms	pesticides, solvents, metals, explosives
Seal Beach Naval Weapons Center	Seal Beach NWC	Seal Beach	pesticides, solvents, metals, explosives

Source: Expenditure Plan for the Hazardous Substance Cleanup Bond Act of 1984 (Revised, January 1987), State of California, Department of Health Services[25]

TABLE 2-14

OPERATIONAL WOOD TREATING FACILITIES IN SOUTHERN CALIFORNIA

Company Name	Facility Location	PCP Usage
J.H. Baxter & Co.	1710 W. 8th Street Long Beach, CA	200 tons/year
San Diego Wood Preserving*	2010 Haffley Avenue National City, CA	40 tons/year

*Not located in the South Coast Air Basin

- Direct optimization of the proposed air monitoring program via modifications to existing methods. The existing approach is predicated on a "target" concentration of 1 pg/m^3, as specified in the bid solicitation. If the literature survey indicates that actual concentrations of PCDDs/PCDFs are well below the pg/m^3 level, then modifications to the sample collection and/or analysis regime may be warranted so as to provide working detection limits commensurate with existing ambient PCDDs/PCDFs concentrations in the South Coast Air Basin.
- Provide an historical data base suitable for comparison to the ambient PCDDs/PCDFs data collected as part of the present air monitoring program.

The discussion to follow will provide a summary of the ambient PCDDs/PCDFs data collected as part of the literature and telephone surveys as well as a discussion on the concept of ambient background (what is it?) and the role that the various types of background data will play in the conduct of the proposed program.

2.5.2 Existing Data Base

<u>Telephone Survey</u>

This survey was designed to gather the most current information on PCDDs/PCDFs in the atmosphere, as well as the most current sampling and analysis protocols suitable for monitoring trace concentrations of PCDDs/PCDFs in ambient air. Direct contact was made with 28 individuals who are actively involved in ambient PCDDs/PCDFs monitoring or data gathering activities. A summary of this information is provided in Table 2-15.

As reflected in the open literature survey, it is apparent that data on ambient concentrations of PCDDs/PCDFs is quite

TABLE 2-15

RESULTS OF TELEPHONE SURVEY - EXISTING DATA ON PCDDs/PCDFs IN THE AMBIENT ATMOSPHERE

NAME	ADDRESS	PHONE	COMMENTS	DATA STATUS
Dr. Ronald Hites	Indiana University School of Public Health and Env. Affairs Bloomington, IN 47405	812-335-0193	Will forward his paper involving ambient monitoring of dioxins.	Data Available Ambient Urban
Frank Lillie Environmental Scientist	EPA New England Research Lab 60 West View Rd. Lexington, MA 02173	617-861-6700	He recommended speaking with Dr. Dave McIntyre, EPA, Lexington.	--
Billy Fairless Chief - Environmental Monitoring and Compliance Branch	EPA 25 Funston Rd. Kansas City, MO 66115	913-236-3884	Will send report containing ambient air dioxin/furan data. Stated that detection limits in the range of 0.5 - 0.7 picograms per cubic meter were obtained. Most samples were BDL. A few were in the 1-7 picogram per cubic meter range. 1 sample was 94 picoggrams per cubic meter. All samples with detectable amounts were taken downwind at the site. Report contains data on an active site, which has been studied for the last two years.	Data Available Times Beach, MO
Dr. Robert Harless	EPA Research Triangle Park, NC 27711	919-541-2248	He recommended speaking with Curtis Ross, EPA Region V, Chicago, and James Sutherland, EPA/RTP, for information.	--
Maxine Jenks Director, Sampling and Analysis	Texas Air Control Board 6330 Hwy. 290 East Austin, TX 78723	512-451-5711	She will send an interim report containing dioxin/furan data obtained from a study at a municipal incinerator. All results were negative. Detection limit in the ppt range. Also did work at Gulf Coast. Again, all results negative.	Data Available MSW
Dr. Tom Tiernan	Wright State University	513-873-2202	Dr. Tiernan stated that he has been doing work with ambient monitoring of dioxins, but cannot release the results at this time, because of confidentiality requirements.	Data Exists Confidential
Douglas Lane	Air Quality and Inter-Env. Research Branch	416-667-4965	Gave the name of Dr. Ray Clement as being Canada's dioxin/furan expert. Dr. Clement works at the Ontario Ministry.	--
Dr. Ray Clement Manager, Dioxin Lab	Ontario Ministry Lab Services Branch P.O. Box 213 125 Resources Rd. Rexdale, Ontario M9W561	416-235-5896	Dr. Clement stated that they are in the early stages of a dioxin monitoring project. A report should be available by the end of the summer. In the meantime, he will forward several papers pertaining to ambient dioxin monitoring that he has found in his own literature search. Dr. Clement recommended calling Dr. Lao and Akos Szakolcai at Air Resources Branch, Canada.	Data Available Sept. 1987
Mike Orbanovsky Environmental Chemist	California Analytical Labs 2544 Industrial Blvd. W. Sacramento, CA 95691	916-372-1393	Could only offer ERT data.	--
Robert Waterfall Sanitation Engineer	NY Dept. of Environmental Conservation (NYDEC) Division of Air Resources 50 Wolf Rd. Albany, NY 12233	518-457-7454	Mentioned ambient monitoring performed in Niagra Falls in conjunction with source testing at Occidental. Referred me to Bill Webster who will be able to produce a copy of the report.	--

TABLE 2-15 (Continued)

NAME	ADDRESS	PHONE	COMMENTS	DATA STATUS
Bill Webster Manager, Ambient Toxic Investigations	NY Dept. of Environmental Conservation (NYDEC) Division of Air Resources 50 Wolf Rd. Albany, NY 12233	518-457-7454	Referred me to Ed Savoi (NY DEC) for data at 518-457-7127.	--
Dave Speece	Environmental Testing Corporation	201-225-5600	Dave recommended I call Mitch Erikson at MRI for information. Dave	--
Dr. Dave McIntyre Senior Environmental Scientist	EPA New England Research Lab 60 West View Rd. Lexington, MA 02173	617-861-6700	Suggested I call Steve Dorrler at EPA, NJ, (Emergency Response Team) at 201-321-6740.	--
James Sutherland Member, Source Analysis Section	EPA Research Triangle Park, NC 27711	919-541-5523	He will send a paper which contains a thorough review of the literature with extensive references pertaining to dioxin sampling. Includes source sampling and ambient monitoring. He recommended I call Gary Amendola, EPA Region V, Westlake, OH for more information.	National Dioxin Strategy
Gary Amendola	EPA 25089 Center Ridge Rd. Westlake, OH 44145	216-835-5200	Gary knows of reports containing ambient dioxin data; one is available now, and one is due out in a few months. The one available now summarizes sampling activities at DOW in Midland, Mi. He is sending me a copy of this report.	Data Available DOW Incinerator
Ed Savoi	NY Dept. of Environmental Conservation (NYDEC) Division of Air Resources 50 Wolf Rd. Albany, NY 12233	518-457-7127	Ed will send out a report which contains ambient dioxin data from sampling at Niagra Falls. He has other data which is unavailable due to confidentiality requirements. He gave the name of Bob Smith at the NY Health Dept. (518-473-3378) as the individual who is familiar with the analytical end of this project.	Data Available OCC Incinerator Other data confidential
Dr. Fred Deroos	Batelle Columbus Laboratories	614-424-6424	Dr. Deroos has ambient dioxin data but is unable to release the data. He suggested I call Dr. Richard Ronen at Versar for release approval, at 703-750-3000.	Data Exists Confidential
Dr. Richard Ronen Vice President	Versar 6850 Versar Center Springfield, VA 22151	703-750-3000	Mark Carkhuff called for Dr. Ronen.	--
Mark Carkhuff	Versar 6850 Versar Center Springfield, VA 22151	703-750-3000	Called for Dr. Ronen. He stated that no data could be released. He suggested I call John Kominsky at NIOSH in Cincinatti for more info.	Data Exists Confidential

TABLE 2-15 (Continued)

LAST NAME	NAME	ADDRESS	PHONE	COMMENTS	DATA STATUS
Kominsky Kominsky Kominsky Kominsky Kominsky Kominsky Kominsky	John Kominsky	NIOSH, Cincinnati	513-841-4382	John stated that he had his own ambient dioxin data, but that it was not available at this time, but would be in several months. He also said that he is presenting a paper at the 7th International Dioxin/Furan Symposium in Las Vegas this October where he will discuss, among other things, ambient dioxin monitoring. He said the detection limit he has achieved in his study is around the 0.1 picogram per cubic meter range.	Data Availbale Oct. 1987-Vegas PCDD/PCDF Symposiu 0.1 pg/m3 LDL
Ross	Curtis Ross	US EPA Region 5, Chicago	312-353-8370	Referred my request to Dennis Wesolowski, EPA Region V.	--
Lao Lao Lao	Dr. Lao Chief Scientist	Environment Canada Ottawa, Ontario CANADA K1A IC8	613-998-3671	No data for one year.	Data Available 1988
Szakolcai Szakolcai Szakolcai Szakolcai	Akos Szakolcai	Air Resources Branch Ontario Ministry of Environment 880 B St., 4th Floor Toronto, CANADA M55 1Z8	416-965-4081	Akos has no data at this time.	--
Wesolowski Wesolowski Wesolowski	Dennis Wesolowski	EPA Region V Central Regional Laboratory Contract Management Section	312-886-1971	Did not have ambient dioxin data. Forwarded my request to Frank Thomas at 312-886-5482, EPA Region V.	--
Dorrler Dorrler	Steve Dorrler	EPA Region II New Jersey	201-321-6740	No data. Steve will see if other individuals in his office has relevant dioxin information.	--
Thomas	Frank Thomas	EPA Region V	312-886-5482	Data exists, but cannot be released at this time.	Data Exists Confidential
Thayil	Boniface Thayil	EPA Region V Air Enforcement Division	312-353-4416	No data.	--

limited. The majority of the available data base identified during the telephone survey can be placed in one or more of the following categories:

- non-detected values (ND) reported in low pg/m^3 concentrations;
- "confidential", and as such are not presently available;
- results consisting of reported values will be available in the near future (e.g. 3-6 months).

Literature Review

A total of seven citations which focused on the distribution and occurrences of PCDDs/PCDFs in ambient air were identified as a result of our literature survey. The majority of these programs consisted of ambient monitoring for selected PCDDs/PCDFs congener classes and/or 2,3,7,8-TCDD in the vicinity of known or suspected area or point sources of these compounds. All the existing literature citations contain data for selected PCDDs/PCDFs congener categories and generally not individual 2,3,7,8-substituted species other than the 2,3,7,8-TCDD isomer.

The New York Department of Environmental Conservation (NYDEC) reported on the results of two one year monitoring campaigns conducted at Niagara Falls and Hempstead, N.Y.[26,27]. Both of these studies focused on measurement of the TCDDs/TCDFs congener classes as well as the 2,3,7,8 TCDD/TCDF isomers. Of a total of twelve samples collected at the Niagara Falls location, four samples contained measurable quantities of TCDFs. One sample contained a quantifiable level of TCDD. The TCDFs values ranged from 1.0 to 13.6 pg/m^3 with an operating sample specific detection limit ranging from 0.06 to 1.0 pg/m^3. The sample that contained 13.6 pg/m^3 total TCDFs also contained 2.1 pg/m^3 of the 2,3,7,8-TCDF isomer. This congener was not observed in any of the other samples.

Only one of the twelve samples contained measurable quantities of TCDDs, and was reported as 1.2 pg/m^3. None of the 2,3,7,8-TCDD congener was observed. Detection limits on a sample specific basis ranged from 0.33 to 4.3 pg/m^3 for the TCDDs congener class. These data which were collected during the calendar period of March 84 to April 85 are reported to represent the "first unambiguous measurement of TCDDs/TCDFs in ambient air in the United States".

Conversely, none of the samples collected at the Hempstead site contained measurable quantities of the target TCDDs/TCDFs. Detection limit were comparable to those provided earlier for the Niagara Falls data set.

Ogle et. al. recently have reported on the results of a preconstruction ambient monitoring program conducted in the vicinity of a proposed resource recovery facility in Hennepin County, Minnesota.[28] As part of the permit requirement ambient background measurements were collected for a series of criteria and non-criteria pollutants at the point of maximum ground level impact downwind of the proposed site location. The non-criteria pollutant portion of the program included monitoring for selected PCDDs/PCDFs for a period of one calendar year prior to operation of a mass feed municipal refuse incinerator. No measureable quantities of PCDDs/PCDFs were observed during the course of the one year program with detection limits reported in the low pg/m^3 range for most of the congener classes. A post-construction monitoring program identical in scope to the initial baseline survey is planned for the near future.

Fairless, et al. recently have reported on the results of an extensive ambient monitoring program conducted in the vicinity of the Quail Run region of the Times Beach Superfund site near St. Louis, Missouri[29]. This program focused exclusively on monitoring of the 2,3,7,8-TCDD congener about the perimeter of the contaminated zone both upwind and downwind during site remediation activities (e.g., soil excavation). Measured concentrations of 2,3,7,8-TCDD were related to both an action level of 3.0 pg/m^3 as well as a calculated no observed effect level of 5.5 pg/m^3. Samples were collected daily with the exception of Sunday. During the calendar period 9/2/85 to 11/1/85, a total of 200 samples were collected and analyzed for 2,3,7,8-TCDD. Ten of those samples contained measurable concentrations of 2,3,7,8-TCDD above the lower limit of detection which ranged from 0.4 - 0.8 pg/m^3. Interestingly enough, none of the ten quantifiable data points were observed at a non-downwind monitor. Each of the reported values occurred on days when site excavation activities were in progress in the vicinity of the monitor. It can be concluded from these data, that the 2,3,7,8-TCDD which was observed during site remediation originated from the site proper, acting as an area source. Additionally, it was concluded from a limited number of samples in which the particulate filter and sorbent cartridge were analyzed separately, that 2,3,7,8-TCDD is associated almost exclusively with particulate matter in ambient air. Conversely, 2,3,7,8-TCDF, as a result of limited spiking experiments, was observed to migrate rapidly from the particulate filter to the sorbent cartridge. It was concluded that since TCDFs appear to be more volatile than TCDDs they "may exist as vapor to a significant extent in ambient air".

Eitzer and Hites reported in March of 1986 what appears to be the most comprehensive data set to date on the occurrences of PCDDs/PCDFs in ambient air.[30] Both rainwater and ambient air samples were collected during the calendar period of March - September 1985 and analyzed for Cl_4-Cl_8 PCDDs/PCDFs. All samples were collected on a third floor terrace of a building situated on the campus of Indiana University in Bloomington, Indiana. Analytical measurements were provided employing a mass spectrometer operating in the electron capture negative ionization mode with methane reagent gas. In each of three sampling sessions conducted, the particulate (filter), vapor (sorbent), and rainwater samples were analyzed separately. Measured concentrations for OCDD ranged from the low fg/m^3 up to 1090 fg/m^3 during the March

12-19, 1985 sampling session. The Cl_4-Cl_8 congener profiles were predominated by the OCDD and TCDFs congener classes. OCDD, which occured both in the vapor and particulate phases, was primarily associated with ambient particulate matter. TCDFs conversely, occurred primarily in the vapor phase, and were observed only with particulate matter during the March sampling session. The majority of the other congener classes which occurred in smaller concentrations followed similar trends intermediate between the distribution extremes noted here for the more volatile TCDFs and the less volatile OCDDs. It can be stated further that the vapor/particle ratio is inversely proportional to both the degree of chlorination and the average temperature during the sample collection period. All congener categories displayed seasonal variations (March, June, September) with respect to the particle/vapor distributions; vapor associated in warmer weather and more affinity for ambient particulate matter in cooler weather. Again, the most critical factor here is the effect of ambient temperature during each respective sampling session.

Lastly, it should be noted that the PCDFs congener profile observed during each of the three sampling sessions very closely approximates the PCDFs congener profiles characteristic of a number of the combustion source categories discussed earlier in Section 2. More specifically, the predominance of the TCDFs congener class in emissions from sewage sludge incinerators and resource recovery facilities may provide some indication as to the source(s) of these components in the ambient air samples reported here.

Summary, Conclusions and Recommendations

Based upon our evaluation of the information gathered during the literature review as well as the telephone survey we would like to offer the following conclusions and recommendations:

- The majority of PCDDs/PCDFs ambient monitoring data in the open literature consists of "ND" values for selected PCDDs/PCDFs positional isomer categories. Detection limits in the low pg/m^3 range are typically provided.
- For those citations which contain actual PCDDs/PCDFs measurements, concentrations in the fg/m^3 ($pg \times 10^{-3}$) are generally reported. These data, as well, are reported for PCDDs/PCDFs positional isomer categories and generally not individual 2,3,7,8-substituted isomers other than 2,3,7,8 TCDD.
- Based upon our review of the available open literature and the recently completed telephone survey, it is ERT's finding that little or no data presently exists on the distribution and occurrences of individual 2,3,7,8-substituted PCDDs/PCDFs isomer in the ambient atmosphere. As a consequence, it is likely that no global ambient background data presently exists for the complete list of 2,3,7,8-substituted PCDDs/PCDFs of interest in the present CARB study.

2.5.3 Background Data Categories (What is Background?)

From an air quality perspective, background is a relative term generally considered to be a measure of the existing concentrations of the components of interest at a specific site or within a given geographical region. These concentrations are in turn a sum or aggregate of all source contributions (e.g., area, point, fugitive, etc.) other than that attributable to the source in question. In order to assess the incremental impacts of any area or point source on air quality in the site vicinity it is imperative that each of several types of background measurements be evaluated. Further discussion pertinent to each of these categories is provided below.

Historical Background Data - Site Specific. This information generally consists of existing air monitoring data specific to the site in question. These data are generally suitable for comparison purposes, but due to disparities in seasonal, temporal, and meteorological parameters as well as incongruities in sampling and analysis procedures, it is not recommended that existing data bases alone be used to establish background concentrations at a given site. These data bases, if available, can provide some indication of existing conditions at the site/facility as well as the historical impact of site specific activities on air quality in the site vicinity.

Historical Data Bases - Geographical Region. In addition to historical air quality data specific to the site itself, some consideration should be given to background data pertinent to the geographical region in which the site is located.

Site-specific and/or Regional Background Data - "Real Time". Naturally, the most important background measurements will be those that assess the relative contribution of the sources to existing air quality in the South Coast Air Basin. Accordingly, three types of background data have been identified as part of the present monitoring program. These include ubran, rural and marine.

Historical Data Bases - Other Geographical Regions

These data bases contain concentrations of PCDDs/PCDFs congeners collected in other geographical regions including urban, rural and "pristine" type areas (e.g. open ocean) where atmospheric concentrations are regarded to be minimum values.

2.6 Sample Collection and Analysis Procedures

A comprehensive review of available sample collection and analysis procedures suitable for ambient monitoring of

PCDDs/PCDFs was conducted as part of the literature review process. Based upon this exercise, as well as information gathered during the aforementioned telephone survey, ERT has concluded that background concentrations of PCDDs/PCDFs in the ambient atmosphere typically are found in the range of 0.01-0.10 pg/m^3 (10-100 fg/m^3). As a consequence of these findings, the sample collection and analysis procedures proposed as part of ERT's response to the CARB solicitation may not be appropriate for such concentration levels. More specifically, it is our anticipation and experience that high-volume air sampling procedures in conjunction with quadrupole mass spectrometry (GC/MS) will likely provide detection limits in the low pg/m^3 (1-5), as specified in our bid response. Alternatively, the use of a magnetic sector mass spectrometer in place of the quadrupole mass spectrometer can be expected to optimize detection limits to the 0.1 pg/m^3 level for the majority of the 2,3,7,8-substituted PCDDs/PCDFs isomers of interest in this program.

3. SITE SELECTION PROCESS

3.1 Overview

Perhaps the most critical component in this or any monitoring program is the selection of the monitoring sites themselves. This is particularly true here since it is essential that the sites selected and the resultant data product represent, as much as possible, existing background conditions with respect to ambient concentrations of PCDDs/PCDFs within the South Coast Air Basin.

This directive in concert with the program objectives offered previously in Section 1, led us to the adoption of a number of primary criteria to be used in the evaluation and selection of "candidate" monitoring sites. Once a number of "candidate" sites had been evaluated and selected for placement within each primary site category, actual monitoring sites were selected on the basis of secondary logistical criteria. These other factors involved in the site selection process include more practical considerations such as the availability of electrical power, site security, and local meteorological data. Subsections 3.2 through 3.4 will address these issues and provide justification for the selection of the list of "candidate" monitoring sites presented in subsection 3.5.

3.2 Site Selection Criteria

3.2.1 Primary Criteria

Particular attention was focused on those sites contained in areas or regions which satisfied one or more of the following criteria:

- Sites within geographical areas or regions which presently contain a concentration of combustion sources and area sources identified in Section 2 as potential emission sources of PCDDs/PCDFs.
- Sites within geographical areas or regions with high population density which also contain a concentration of potential PCDDs/PCDFs emission sources.
- Sites within geographical areas or regions of high population density which do not presently contain known PCDDs/PCDFs emission sources but in which a known number of these sources are proposed for location in the near future.
- Background (Urban) - Sites within geographical areas or regions with high population density which do not contain any of the potential PCDDs/PCDFs emission sources either existing or proposed, as identified earlier.
- Background (Rural) - Sites within geographical areas or regions with low population density and no known or potential sources of PCDDs/PCDFs emissions.
- Background (Marine) - Sites situated offshore west of the mainland of the South Coast Air Basin with little or no population and no clearly identifiable potential PCDDs/PCDFs emissions sources. It is anticipated that such a site or sites will provide an indication of "true" ambient baseline and perhaps an indication of global concentrations of PCDDs/PCDFs that can be expected in a near "pristine" environment.

Further details on each of these primary siting criteria, including the actual locations of regions that satisfy the above classifications, are provided in the discussion to follow. This includes supporting data on the actual locations of existing or proposed combustion sources, existing area sources as well as population density data plotted using the most recent census data for the South Coast Air Basin.

3.2.2 Secondary Criteria

In addition to the primary site selection criteria stated above, secondary criteria, primarily involving logistics must also be considered. These criteria include such things as availability of electrical power for the operation of the required samplers, the availability of site security to insure the integrity of the samples collected, and the availability of on-site and local meteorological data including wind speed, wind direction, temperature, and if possible, barometric pressure, relative humidity, and precipitation. In the process of selecting potential sampling site locations, once the appropriate primary criteria had been satisfied, "candidate" sites were evaluated and prioritized, or ranked, on the basis of the aforementioned secondary criteria.

3.3 Potential Source Locations in the South Coast Air Basin

3.3.1 Combustion Sources

Major potential combustion sources of PCDDs/PCDFs include hazardous waste incinerators, refuse-to-energy plants, sewage sludge incinerators, hospital incinerators, and wire reclamation operations. Exhibit 1, found in the pocket of this document, depicts the locations of proposed and existing resource recovery facilities, hazardous waste incinerators, waste-to-energy projects, sludge incinerators, and biomass-to-energy facilities in the South Coast Air Basin.

Additionally, the locations of known hospital incinerators and wire reclamation incinerators are listed in Tables 2-9 and 2-11 of this document. The locations of these incinerators were taken from the emission inventory data supplied to ERT by the South Coast Air Quality Management District (SCAQMD). The complete inventory is located in Appendix I of this report.

3.3.2 Area Sources

Categories of potential PCDD/PCDF area sources in the South Coast Air Basin include known hazardous waste sites, landfills (in particular those known to contain PCDDs/PCDFs containing wastes or chlorinated precursors), wood treating facilities, active landfills which accept ash residues from any of the combustion sources described in subsection 3.3.1 (above), agricultural burning, pesticide formulating operations, and automobile emissions. The locations of known wood treating facilities, hazardous waste sites, and pesticide formulating plants are listed and described in subsection 2.4 of this document.

3.3.3 Background Sites

As discussed previously in Section 2.5.2 it is ERT"s belief that background or "baseline" data is an integral component of any ambient monitoring program as it provides a basis to assess what impact, if any, potential PCDDs/PCDFs emission sources presently have on air quality in the affected region(s). Additionally, such data will provide a statistical basis for future data comparisons in assessing the incremental impacts attributable to the addition of new sources to a particular region at a future date.

In accordance with the site selection criteria offered earlier, background sites should represent, to the extent possible, each of three source classifications; namely rural, urban, and marine. Actual monitors are placed within each region out of areas impacted by existing point sources or fugitive emission area sources.

3.4 Population Density

One of the main objectives of this sampling and analysis program is to assess the exposure of segments of the general population of the South Coast Air Basin to concentrations of PCDDs/PCDFs in the atmosphere. Site selection then, should make use of population density data. Exhibit 2, found in the pocket of this document, depicts the population density of the South Coast Air Basin. This information, which ERT understands to represent the most recent census data for the South Coast Air Basin, was most instrumental in the definition of each of the areas or regions notes in Section 3.2, as well as the evaluation and selection of "candidate" monitoring sites within each region. The population density data, accordingly, was a major factor in the primary site selection criteria offered earlier.

3.5 Selected "Candidate" Monitoring Sites

Eleven "candidate" monitoring sites, listed in Table 3-1 and depicted in Figure 3-1 have been selected based on the primary and secondary selection criteria detailed in the proceeding subsections of this document including combustion and area source locations, population density data, and practical considerations including power and security availability and availability of local meteorological data. Many of the selected sites are existing South Coast Air Quality Survey (SCAQS) sites and therefore have the advantage of meeting all of the secondary criteria.

By using all or most of these sites during the course of the program, a representative background data base can be provided commensurate with the aforementioned program objectives. In addition, it will be comparable to other air monitoring data concurrently collected at each of the respective sites as part of other on-going air quality investigations already in place (e.g. SCAQS Program).

TABLE 3-1
"CANDIDATE" MONITORING SITE LOCATIONS - SOUTH COAST AIR BASIN

SITE	ADDRESS	SCAQS PARTICIPANT	PRIMARY CRITERIA						SECONDARY CRITERIA			COMMENTS
			COMBUSTION SOURCE	AREA SOURCE	POPULATION EXPOSURE	URBAN BACKGROUND	RURAL BACKGROUND	MARINE BACKGROUND	POWER AVAILABLE	SECURITY AVAILABLE	METEORLOGICAL DATA AVAILABLE	
ANAHEIM	1010 S. HARBOR BLVD.	YES		X	X				X	X	X	
BURBANK	288 WEST PALM AVE.	YES			X	X			X	X	X	
BURBANK	272 E. OLIVE AVE.	NO			X	X			X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
AZUZA	803 N. LOREN AVE.	YES	X	X					X	X	X	
HAWTHORNE	5234 W. 120TH ST.	YES	X	X					X	X	X	
EL MONTE	9528 TELSTAR AVE.	NO		X	X				X	X	X	TEMPORARY STATION OPERATED BY CARB
LOS ANGELES	1630 N. MAIN ST.	YES	X	X	X				X	X	X	
LOS ANGELES	430 E. 7TH ST.	NO	X	X	X				X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
LONG BEACH	LONG BEACH CITY COLLEGE	YES	X	X	X				X	X	X	
POMONA	POMONA COLLEGE	YES	X	X					X	X	X	
IRVINE	15029 SAND CANYON	NO					X		X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
RIVERSIDE	5888 MISSION ST., RUBIDOUX	YES		X					X	X	X	
SAN NICHOLAS IS.		YES						X	X	X	X	

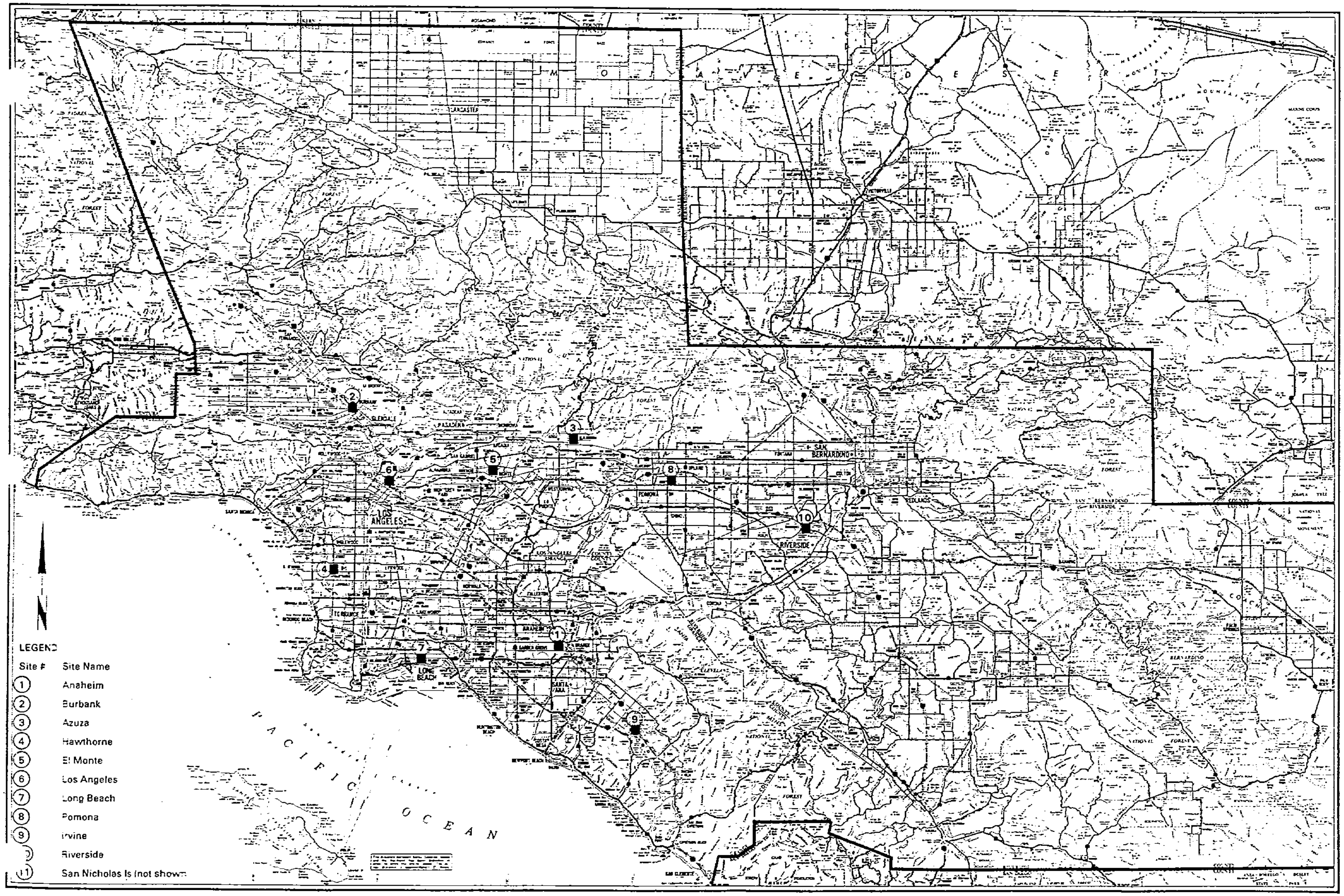

Figure 3-1 "Candidate" Monitoring Sites

4. MONITORING NETWORK DESIGN

4.1 Site Locations

ERT expects that all of the "candidate" sites listed in Table 3-1 will be sampled during the initial phase of the monitoring program. Later, five to seven of the "candidate" site locations will be selected for sampling during the extended monitoring program. The selection of which particular sites will be chosen will be based primarily on two factors. First priority will be for the sites representing each of the primary criteria from which measureable concentrations of PCDDs/PCDFs were detected during the first round of sampling and analysis. Secondly, sites which have been determined to be most representative of the program objectives will be selected.

It is anticipated that the extended monitoring network will be comprised of sites which represent two combustion sources, one area source, two areas of high population densities, and two background locations. Table 4-1 lists each of the source categories and the number of sites expected per category for the extended monitoring portion of the program.

4.2 Sampling Schedule and Frequency

It is anticipated that a total of five sampling periods will be conducted for each of the sites identified in Table 4-1. These five sessions will be conducted at approximately equivalent time intervals over the course of the extended monitoring program. In addition, during each of the prescribed sampling periods, collocated samplers and field-biased blanks will be collected as requisite quality control measures. As a result, approximately 50 samples will be submitted to ENSECO-CAL for PCDD/PCDF analyses. Of this total, approximately 30 percent, or 15 samples, will represent field-biased blanks and collocated samples. A total of 13 samples from the background category are also included in the

TABLE 4-1

SITE SELECTION, DISTRIBUTION, AND MONITORING FREQUENCY

SOURCE CATEGORY	# OF SITES PER CATEGORY	# OF SAMPLING PERIODS PER SITE	TOTAL SAMPLES PER CATEGORY	QA/QC SAMPLES PER CATEGORY*	TOTAL AIR SAMPLES
COMBUSTION SOURCE	2	5	10	5	15
AREA SOURCE	1	5	5	2	7
POPULATION BIASED	2	5	10	5	15
BACKGROUND	2	5	10	3	13
TOTAL	7	5	35	15	50

* Includes both field-biased blanks and collocated samplers

total of 50. Section 7 of this document includes a discussion of the evaluation criteria of the collected field samples to determine which of the samples will undergo actual laboratory analysis.

It is anticipated that each sampling session will be conducted over an approximate 24-hour period to accommodate diurnal variations at each site. However, as is discussed in Section 6.3 of this document, the sampling period may be extended up to 48 hours in length if it is determined during the initial phase of monitoring that a larger sample volume is necessary to achieve measureable results based on the appropriate analytical detection limit. All samplers will be operated concurrently during each sampling session.

5. METEOROLOGICAL MONITORING

5.1 Overview

Representative meteorological monitoring data will be collected during all sampling periods at or as near as practicable to each sampling site. It is our anticipation that many of the "candidate" sites identified in Section 3 will have direct access to real-time, site specific meteorology. This is particularly true in the case of those sites that are contained in the aforementioned SCAQS network. Every effort will be made to collect samples during periods in which the existing site specific meteorological system is in operation.

For those sites which do not have dedicated site meteorology or in instances where the existing system is not accessible to us, ERT will make use of portable meteorological monitoring systems.

In all instances, meteorological measurements will include, at a minimum, wind speed wind direction, and ambient temperature and also barometric pressure if possible. All data will be recorded on strip charts or accumulated by a data acquisition system, and then digitized into 1-hour averages during the course of the sampling program. Further details on both the permanent and portable meteorological collection systems are provided below.

5.2 Permanent Site Meteorology

Many of the selected sampling sites for this program have existing meteorological monitoring instrumentation in operation at the site or are located where meteorological data is currently collected in the nearby vicinity. Table 5-1 lists the sample collection sites, the locations of representative meteorological data for each site and the categories of meteorological data collected. Permanent meteorological monitoring sites will be evaluated on their compliance with the

TABLE 5-1

METEOROLOGICAL MONITORING DATA COLLECTION

CANDIDATE SAMPLING SITE	ADDRESS	METEOROLOGICAL MONITORING SITE LOCATION	AVAILABLE METEOROLOGICAL DATA		
			WIND SPEED	WIND DIRECTION	TEMPERATURE
ANAHEIM	1010 SOUTH HARBOR BLVD.	ON SITE	X	X	
BURBANK	288 WEST PALM AVENUE	ON SITE	X	X	
BURBANK	272 EAST OLIVE AVENUE	ON SITE	X	X	
AZUSA	803 NORTH LOREN AVENUE	ON SITE	X	X	
HAWTHORNE	5234 WEST 120TH STREET	ON SITE	X	X	
EL MONTE	9528 TELSTAR AVENUE	ON SITE	X	X	
LOS ANGELES	1630 NORTH MAIN STREET	ON SITE	X	X	
LOS ANGELES	430 EAST 7TH STREET	ON SITE	X	X	
LONG BEACH	LONG BEACH CITY COLLEGE	ON SITE	X	X	X
POMONA	POMONA COLLEGE, FOOTHILL BLVD.	ON SITE	X	X	X
IRVINE	15029 SAND CANYON	ON SITE	X	X	
RIVERSIDE	5888 MISSION ST. (RUBIDOUX)	ON SITE	X	X	
SAN NICHOLAS IS.		ON SITE	X	X	

guidelines found in the EPA Quality Assurance Handbook for Air Pollution Measurements Systems; Volume IV - Meteorological Measurements (EPA-600/4-82-060. and will include, at a minimum, hourly and daily averages of wind speed and wind direction. If possible, ambient temperature and barometric pressure will also be collected.

5.3 Portable Meteorological Monitoring

At sites where no representative or dedicated meteorological data exists, a portable meteorological monitoring system will be employed.

The meteorological monitoring instruments used in this case will be the Climatronics EWS electronic weather station, or its performance equivalent. The Climatronics EWS is designed to measure, display, and record wind speed and wind direction on a continuous basis. The unit is portable and fully self contained, and operates on either 120 VAC or 12 VDC power. The sensor and recorder specifications (shown in Table 5-2) meet or exceed the guidelines suggested in the EPA Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV Meteorological Measurements (EPA-600/4-82-060). Figure 5-1 depicts the Climatronics EWS system.

5.4 Laboratory Calibration and Maintenance

Prior to committing the Climatronics EWS to field service, all preventative maintenance and calibration checks will be completed in the laboratory. Preventative maintenance will be completed following the manufacturer's recommendations. Calibration will be completed following the technical instruction found in Appendix B of this document.

TABLE 5-2

METEOROLOGICAL INSTRUMENTATION SPECIFICATIONS

Sensor Specifications

Sensor	Accuracy	Range	Distance or Time Constant	Threshold	Damping Ratio
WS	±0.25 mph	0-100 mph	8 ft max	0.75 mph	--
WD	±1.5%	0-360° Mech. 0-540° Elect.	8 ft max	0.75 mph	0.4-0.6

Recorder Specifications

Sensor	Range	Chart Resolution
WS	0- 50 mph 0-100 mph	± 0.5 mph
WD	0-540°	±5°

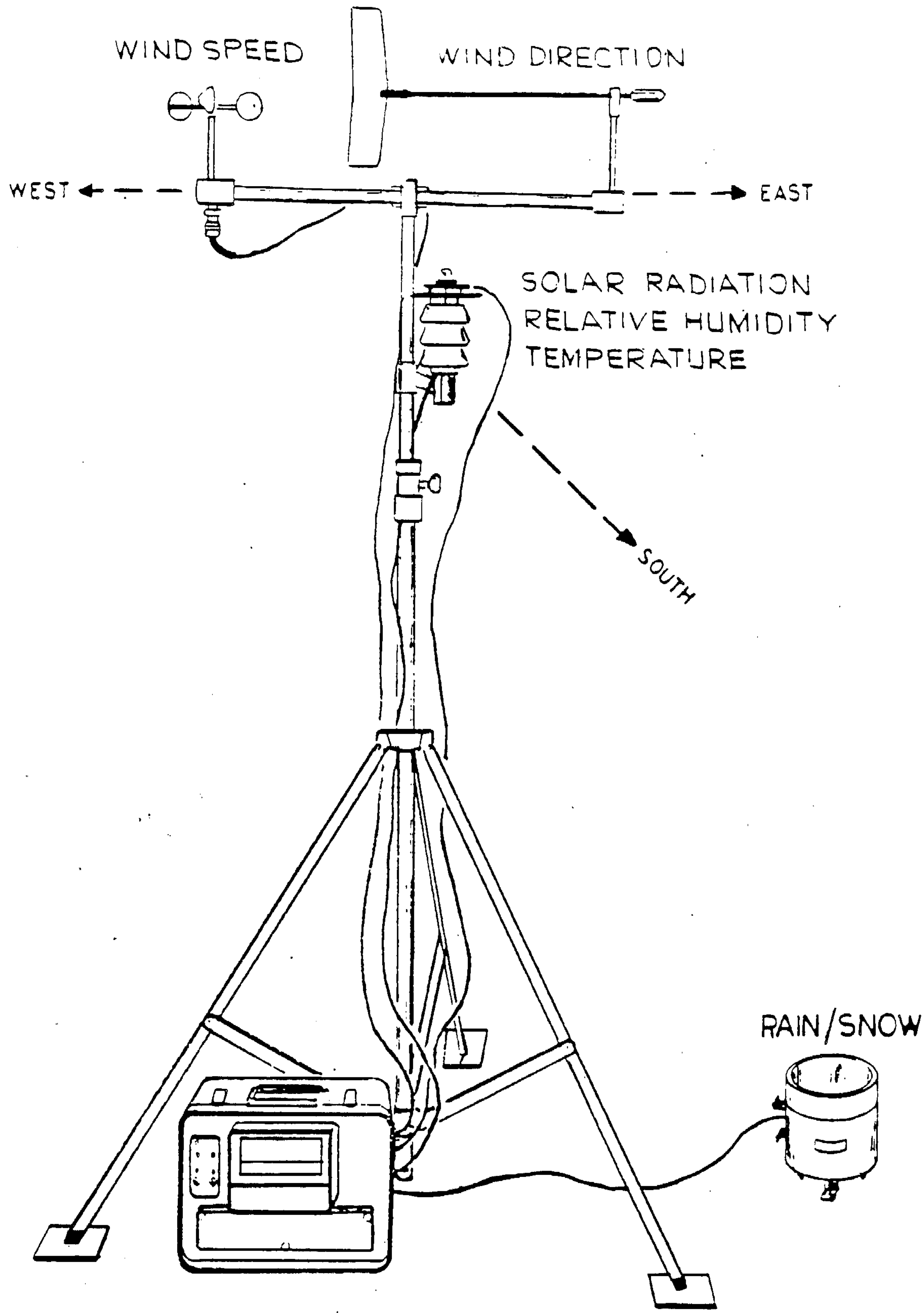

Figure 5-1   Typical Electronic Weather Station Configuration

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5.5 Field Installation and Calibration

After the meteorological monitoring station site location is chosen, the system will be installed and field calibrated following the Standard Operating Procedure found in Appendix B of this document.

5.6 Field Operation

After field installation and calibration, the meteorological monitoring equipment will be operated by following the Standard Operating Procedure found in Appendix B of this document.

6. SAMPLE COLLECTION PROCEDURES

6.1 Overview

Ambient air samples will be collected at selected monitoring sites using General Metal Works Model PS-1 sorbent samplers in accordance with the sample collection schedule and frequency specified earlier in Section 4.2. The samplers will be fully calibrated prior to and at the completion of each sampling session and "spot checked" during each prescribed sampling period. The sample collection system, as well as calibration and operation procedures and expected flow rates and sampling durations, are described below. The actual sample collection regime employed by ERT is consistent with the approach contained in EPA Method T09 provided in Appendix H of this document.

6.2 Sample Collection System

Selected polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDDs/PCDFs) isomers which include all fifteen 2,3,7,8 congeners listed in Table 1-1, will be collected by use of the General Metal Works Polyurethane Foam (PUF) sampler (PS-1). The PS-1 is basically a modified high-volume air sampler which employs both a glass fiber filter and a sorbent trap to collect semi-volatile organic compounds associated with particulates as well as those in the vapor state. The General Metal Works PS-1 sampler, depicted in Figure 6-1, is equipped with a by-pass blower motor arranged with an independent cooling fan. This feature permits the motor to operate at low sampling flow rates for periods of long duration without motor failure from overheating. The sampling module contains two chambers. The upper chamber supports the particulate filter media, and the second chamber contains a glass cartridge containing a plug of polyether-type polyurethane foam (PUF) which has been cleaned and prepared as described in Section 8 of this document. A typical PUF sampling cartridge is depicted in Figure 6-2.

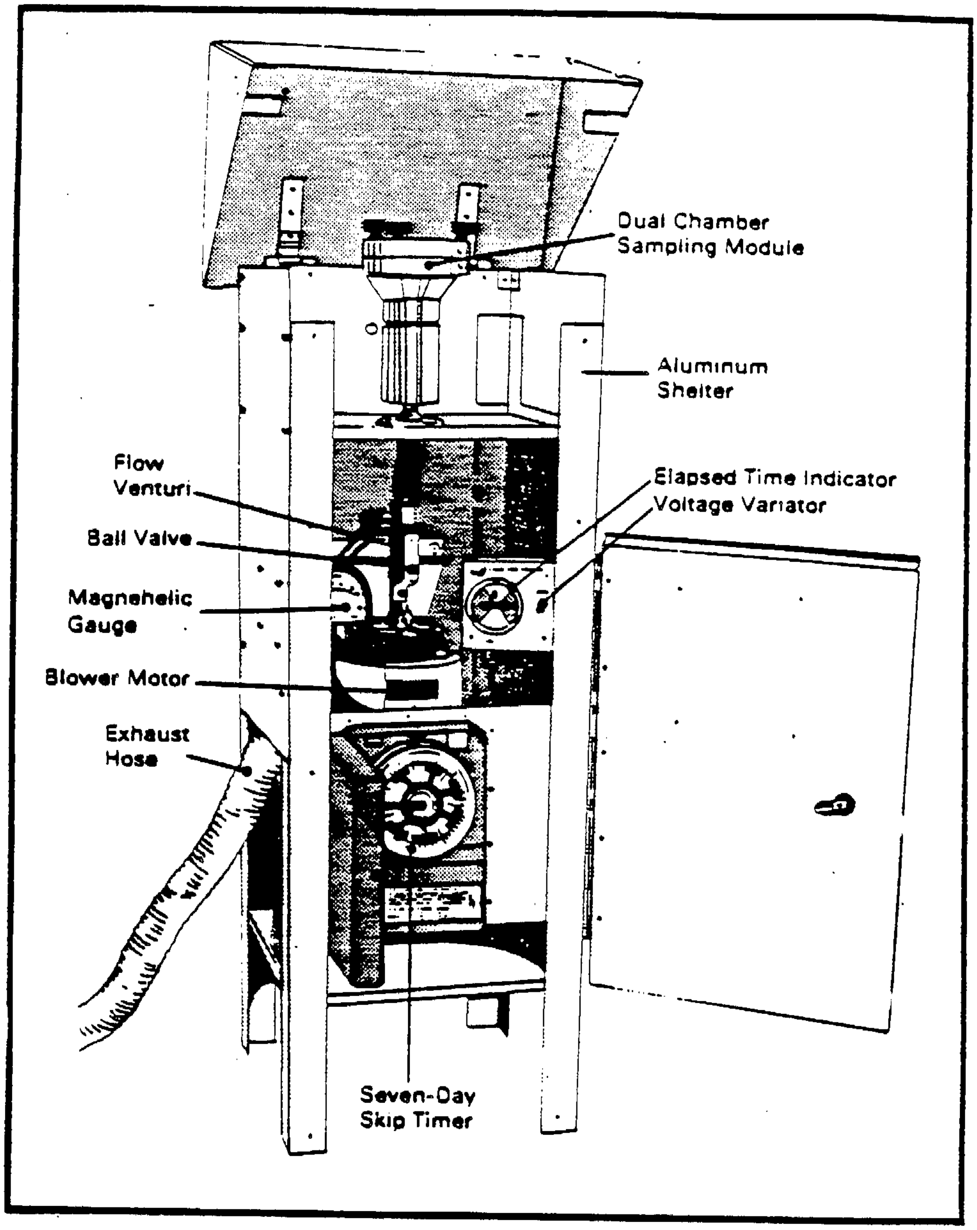

Figure 1a
Sampler

Figure 1b
Dual Chamber
Sampling Chamber

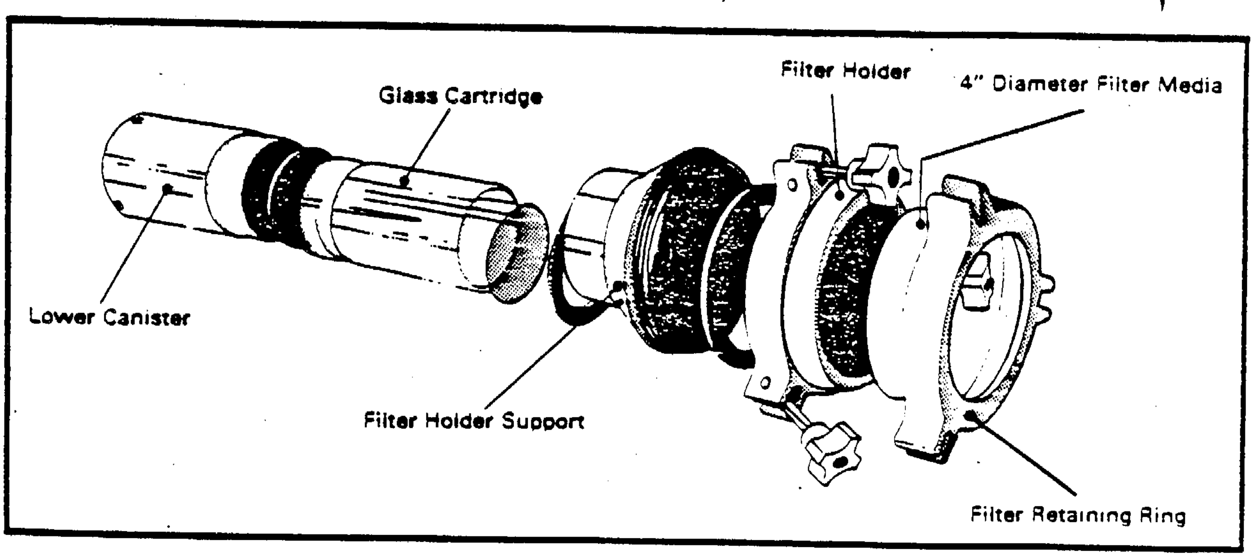

Figure 6-1 Schematic of PS-1 Sampler

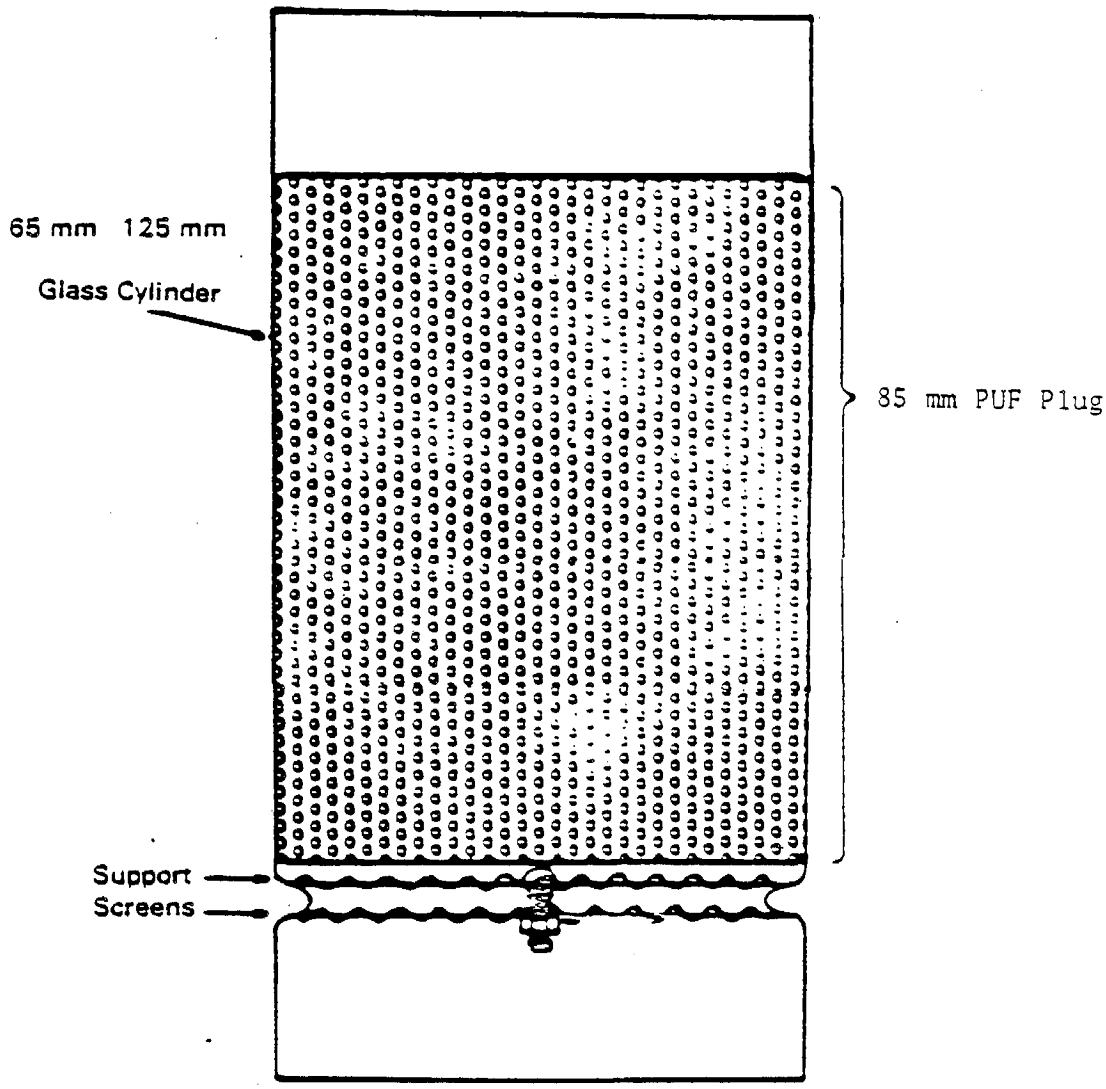

Figure 6-2 PUF Sampling Cartridge

Air flow rates are variable up to 280 liters per minute and the unit is also equipped with a 7-day timer, magnehelic flow gauge, voltage variator, and elapsed timer.

6.3 Calibration

The PS-1 samplers will be calibrated by ERT prior to and at the conclusion of each sampling session. Calibration will be conducted as specified in ERT SOP 2620-300 which is included in Appendix C of this document.

6.4 Sampling Parameters

6.4.1 Sample Collection Flows and Volumes

As detailed in Section 2.5, it is anticipated that ambient PCDDs/PCDFs concentrations present in the South Coast Air Basin are likely to occur in the fg/m^3 range (e.g., 10-100 fg/m^3), particularly in the case of the individual 2,3,7,8-substituted congeners. This is anticipated as a result of the literature survey conducted as part of the Phase I work scope. As a consequence, optimal detection limits can only be achieved through the use of higher than normal air volumes in conjunction with high resolution mass spectrometry (HRMS). The former condition can be met by a combination of increased sampler flows (lph) and/or sampling intervals extended beyond the nominal 24 hour period suggested in ERT's proposal document. (The use of high resolution mass spectrometry as a means to enhance sensitivity is discussed in more detail in Section 8).

ERT's customary approach to sample collection consists of a 24 hour sampling interval at an air collection flow of 200-280 lpm. This results in total collection volumes ranging from 288-400 m^3. Based upon absolute analyte sensitivities for HRMS provided to us by ENSECO-CAL laboratories, it is anticipated that the lower limits of sensitivity provided in

Table 6-1 for each of the 15 congeners can be achieved. As noted, these values assume an upper limit air volume of 400 m^3, which is achievable via a 280 lpm flow over a 24 hour sampling period. This approach is consistent with the sample collection protocol contained in EPA Method T09 provided in Appendix H of this plan, which prescribes a sample collection volume of 325 m^3.

It is recommended, therefore, that samples from the first sampling session be collected at a flow rate of 280 lpm for a 24 hour (1440 minutes) period to obtain a total sample volume of approximately 400 m^3. This approach will be evaluated after results from the first sampling session become available. If no measurable concentrations of the "target" PCDDs/PCDFs congeners are found at or near the sensitivity goals stated in Table 6-1 in any of the samples, then extension of the sample collection period up to 48 hours may be warranted. If at this stage, after consultation with the CARB, it is decided that lower limits of sensitivity are desired, then ERT will extend the sample collection period to 48 hours for the next sampling session. It is anticipated that a 48 hour sampling period in conjunction with the analytical sensitivities provided earlier will result in the lower detection limits provided in Table 6-1.

6.4.2 Breakthrough Considerations

It should be noted, however, that there is no data presently available to our knowledge to indicate that component breakthrough would not occur from the prescribed sorbent cartridge in the collection of an 800 m^3 sample. EPA T09, for instance, indicates that breakthrough has not shown to be a problem with sampling volumes of 325 m^3. Should the requisite to collect 800 m^3 or greater sample volumes arise, then it is recommended that additional measures be taken to insure that analyte breakthrough is not a factor. This would entail analysis of the PUF sorbent cartridge in sections (2

TABLE 6-1

PCDD/PCDF ISOMER DETECTION LIMITS

(HIGH RESOLUTION GC/MS)

	Anticipated Detection Limit		
	pg/sample	fg/m3 @ 400 m3 total volume	fg/m3 @ 800 m3 total volume
PCDD Isomer			
2,3,7,8 TCDD	5	12	6
1,2,3,7,8 PeCDD	15	36	18
1,2,3,6,7,8 HxCDD	10	24	12
1,2,3,7,8,9 HxCDD	10	24	12
1,2,3,4,7,8 HxCDD	10	24	12
1,2,3,4,6,7,8 HpCDD	10	24	12
PCDF Isomer			
2,3,7,8 TCDF	5	12	6
1,2,3,7,8 PeCDF	10	24	12
2,3,4,7,8 PeCDF	10	24	12
1,2,3,6,7,8 HxCDF	5	12	6
1,2,3,7,8,9 HxCDF	5	12	6
1,2,3,4,7,8 HxCDF	5	12	6
2,3,4,6,7,8 HxCDF	5	12	6
1,2,3,4,6,7,8 HpCDF	10	24	12
1,2,3,4,7,8,9 HpCDF	10	24	12

or 3) to assess the % loading of each analyte within each of the cartridge sections. If significant breakthrough or component loss is observed, then actual sample collection volumes will be reduced accordingly for subsequent sampling sessions.

It is also possible that experimental data may be available within the next couple of months which validates the sampling protocol for use in the collection of air samples up to 1000 m^3 in volume. This work, which is being conducted by ERT, if successful will permit us to dispense with the analyses of sorbent sections as a means to assess component "breakthrough".

6.4.3 Surrogate Spikes

An additional measure of program quality control will consist of the use of isotopically labeled surrogates applied to the "head" of each PUF sorbent cartridge prior to commencement of the sample collection sequence. It is anticipated that 50 pg each of two surrogates (Cl^{37} - 2,3,7,8-TCDD and C_{13} - 1,2,3,4-TCDD) will be applied to every field sample as a measure of precision for the combined sample collection and analysis regime. These data will also serve to monitor the tendency for analyte breakthorugh within each program sample as the surrogates are applied prior to sample collection.

6.5 Sample Shipping and Handling Procedures

All sample filters and cartridges will be prepared and packaged for field use at the laboratory prior to shipment to the monitoring sites as per the applicable procedures found in the appendices of this document. The cartridges will be contained in field sampling kits and packaged in shipping coolers. When used for sampling, the cartridges will be handled only with clean, cotton gloves. After sampling has been completed, the cartridges will be packaged back in their original containers, wrapped in bubble wrap or soft paper, and packed "snugly" in coolers with dry ice. The sample coolers will be shipped as soon as possible to the laboratory sample bank. All samples will be extracted within 7 days of collection, and analyzed within two weeks of extraction.

6.6 Sample Chain-of-Custody and Documentation

Sample control, including chain-of-custody and documentation procedures, is essential to this program. Chain-of-custody procedures serve two purposes:

- They provide a mechanism for assignment of responsibility for sample integrity.
- They provide physical evidence of the history and integrity of each sample, from collection through analysis and data reporting.

Documentation procedures include mechanisms to assure the use of proper sample handling and proper labeling and tracking from sample media preparation in the laboratory through sample collection, and transportation to the laboratory sample bank. Detailed sample control and chain-of-custody procedures can be found in the Quality Assurance Project Plan (Section 9) and the appendices of this document.

7. EVALUATION CRITERIA FOR THE SELECTION OF FIELD SAMPLES FOR ANALYSES

As discussed previously, approximately 50 to 70 samples will be collected for PCDDs/PCDFs. Not all of the samples collected, however, will be selected to undergo analyses. It has been ERT's experience that redundancy or multiplicity of sample sets provides us with much needed flexibility in the selection of samples for analysis. For example, only those samples with the highest probability of providing useful, defensible, representative data of the highest quality will be prioritized for analyses. In this manner we can provide a high-quality, more cost-effective approach while at the same time a means to eliminate "suspect" samples of poor quality or diminished integrity. A summary of the pertinent evaluation criteria employed in the selection/prioritization of field samples for laboratory analyses is provided in Table 7-1.

TABLE 7-1

EVALUATION CRITERIA FOR THE SELECTION/PRIORITIZATION OF FIELD SAMPLES FOR LABORATORY ANALYSES (PRIORITY GIVEN TO SAMPLES SATISFYING CRITERIA PROVIDED BELOW)

Category	Criteria
Meteorology	1. Consistent prevailing wind patterns during sampling session (e.g. wind direction). 2. Absence of precipitation during sampling session. 3. Monitoring Site Location consistent with wind direction (upwind and downwind). 4. Seasonably moderate to warm temperatures.
Sampler Operation	1. Pre and post flow calibration checks in good agreement (<10% difference). 2. No visible signs of "tampering" during sampling session.
Sample Physical Integrity	1. No physical signs of damage (e.g. cracks, other defects) in sorbent cartridge upon receipt at laboratory.
Sample Documentation	1. No ambiguities in sample identification, chain-of-custody, etc., Sample ID tag; other records in good agreement.

8. ANALYTICAL PROCEDURE

8.1 Overview

All samples will be shipped directly from the field under chain-of-custody to ENSECO-CAL Laboratory in Sacramento, CA for analysis. All samples will subsequently undergo analysis for each of the fifteen 2,3,7,8-substituted PCDDs/PCDFs congeners listed previously in Table 6-1 employing combined gas chromatography/mass spectrometry (GC/MS).

It was ERT's original position as stipulated in our proposal, as well as during the initial stages of Phase I of the program, that all GC/MS analyses would be conducted employing low resolution or quadrupole mass spectrometry exclusively. However, based upon the results of the literature survey provided in Section 2.5, as well as our own recent experience, it is our present feeling that target sensitivities in the 10-100 fg/m^3 may be required so as to accommodate likely existing concentrations for each of the PCDDs/PCDFs congeners in ambient air.

As a consequence, it is our recommendation that high-resolution or magnetic sector mass spectrometry be selected in place of the low resolution or quadrupole option. The analytical methodology employed by ENSECO-CAL essentially represents a modified version of EPA Method TO9 entitled Method for the Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDS) in Ambient Air Using High Resolution Gas Chromatography/ Mass Spectrometry released in September, 1986. A copy of EPA Method TO9 is provided in Appendix H of this document. While the HRMS method may appear more suitable for accommodating PCDDs/PCDFs concentrations likely to exist at the present time in the South Coast Air Basin, we offer both the low resolution and the high resolution methodologies in Section 9 and the appendices to follow, so as to provide the CARB technical review committee the opportunity to evaluate both of these analytical approaches. A summary of each analytical component within each of these approaches is provided in the discussion to follow. This includes the sample preparation procedures, which are common to both, as well as a summary of the two mass spectrometry approaches.

8.2 Sample Preparation Procedures

8.2.1 Combined Particulate/Sorbent Samples

Each sample consisting of a combined particle filter and sorbent cartridge is spiked with C_{13} isotopes of Cl_4-Cl_7 dioxins, Cl_4 furans and ^{37}Cl-2,3,7,8-TCDD and then soxhlet extracted with benzene for 16 hours. Sample clean-up is accomplished using several single and mixed phase liquid chromatography columns. The first is an IFB/Acid alumina column which consists of a mixed phase acidified/basic silica gel column followed immediately by acid alumina. A silica gel/charcoal mixed phase micro column is also used in the sample clean-up process. A third optional column utilized is a mini-column of basic alumina. In between each clean-up step the eluant of interest is concentrated to a volume of approximately 1 ml. The final extract is in tetradecane and taken to a final volume of 10-50 ul. After sample preparation, the sample extracts are analyzed by GC/MS. The actual text of all sample preparatory procedures are provided in the ENSECO-CAL Standard Operating Procedures (SOPs) provided in Appendices F and G of this document.

8.2.2 Particulate and Sorbent Samples Analyzed Separately

As noted previously in Section 2.5, existing data for PCDDs/PCDFs in ambient air consist almost exclusively of measurements representing the particle and vapor phases combined. The sample preparation scheme discussed in Section 8.2.1 assumes that the majority of the samples processed as part of the present program will be treated in the same manner.

However, as proposed by ERT in our original bid response and acknowledged by CARB in the written contract, a select number of samples will undergo analysis of the particulate filter and sorbent cartridge separately. Six actual samples will be treated in this manner. These will most likely consist of collocated samples selected on the basis of PCDDs/PCDFs being detected in the other member of each collocated sampler pair.

In each instance, the particulate filter and the sorbent cartridge will be processed separately, and analyte concentrations will be reported as fg/m^3 vapor phase and fg/m^3 particle-associated. The surrogate mixture consisting of the isotopically labeled C_{13}, ^{37}Cl congeners noted in 8.2.1 will be split such that certain congeners are applied directly to the particulate filter and the remaining congeners are applied as in 8.2.1 to the sorbent cartridge just prior to commencement of the sample preparation or extraction sequence. Analyses beyond this point including extract concentration, clean-up and GC/MS analysis will proceed in an identical manner to the combined particulate/sorbent samples.

8.3 Gas Chromatography/Mass Spectrometry (GC/MS)

Dioxin and furan analysis by GC/MS involves a preliminary screening analysis employed to ascertain total dioxin/furan levels in the sample. If this procedure indicates the presence of dioxins/furans, then further GC/MS analysis will be performed to determine levels of the fifteen 2,3,7,8-Cl_4-Cl_7 isomers listed in Table 6-1. The analytical protocols employed for these determinations are described in the following sections.

8.3.1 Quadrupole Mass Spectrometry (Low Resolution)

Total Cl_4-CL_7

- GC Parameters - Analysis for total Cl_4-Cl_7 dioxins and furans is carried out by injecting a 1-2 ul sample onto a DB-5 column employing the GC conditions specified in Table 8-1. Mass chromatograms for all the Cl_4-Cl_7 dioxins/furans monitored masses are generated. In addition, suspected 2,3,7,8-substituted isomers are flagged.
- Instrument Calibration - Calibration is carried out by running 2 ul of 0.5 ng DB-5 column performance check mix containing the following TCDD isomers: 1,3,6,8-, 1,2,8,9-, 1,2,3,4-, 2,3,7,8-, 1,2,3,9- and 13C12-2,3,7,8-TCDD. In addition, running 2 ul of dioxin and furan window defining mix, 3 PCDD/PCDF standard mixes (concentrations 0.2 to 1.0 ng/m) and a blank sample or solvent blank is required before running any samples.

TCDD/TCDF Only

- GC Parameters - Analysis of the 2,3,7,8- substituted isomers of Cl_4-Cl_7, as listed in Table 6-1 is carried out using a SP-2331 column and GC parameters described in Table 8-1. 1-2 ul of sample are analyzed and only the specific 2,3,7,8-substituted isomers are calculated. These results are compared to the DB-5 data to check for consistency.
- Instrument Operation - Standards and samples are analyzed with the mass spectrometer operating in the selected ion monitoring (SIM) mode using a scan time which gives at least five parts per peak.

TABLE 8-1

RECOMMENDED GC OPERATING CONDITIONS

Column	60 meter (SP 2331)	60 meter DB-5	30M DB-225
2,3,7,8-TCDD R.T.	12 min	10.0 min	11.0 min
Helium Linear Velocity		30 cm/sec	
Initial Temperature	190 C	190 C	190 C
Initial Time	1 min	1 min	1 min
Splitless Time	0.6 min	0.5 min	1.0 min
Program Rate	10 C/min	8 C/min	8 C/min
Final Temperature	250 C	300 C	240 C
Final Hold Time	15 min	7 min	7 min
Split Flow	30 ml/min	30 ml/min	30 ml/min
Septum Purge Flow	5 ml/min	5 ml/min	5 ml/min
Capillary Head Pressure	28 psi	15 psi	15 psi

The above GLC conditions are employed for both classification and the isomer specific analysis of tetra through octa chlorodioxins and dibenzofurans.

The 60 meter DB5 is appropriate for total C14-C18 D/F classification. Isomer specific analysis of all 2,3,7,8-substituted chlorinated dibenzodioxins and dibenzofurans required a 60 meter DB-5 and a 60 meter SP 2331. If 2,3,7,8-TCDF is suspected it must be analyzed as well on DB-225.

- Instrument Calibration - Calibration is carried out by running 2 ul of 0.5 ng DB-5 column performance check mix containing the following TCDD isomers: 1,3,6,8-, 1,2,8,9-, 1,2,3,4-, 2,3,7,8-, 1,2,3,9-, and 13C12-2,3,7,8-TCDD. A 4 point standard curve is run over a concentration range of 10 pg to 100 pg. In addition, a method blank or solvent blank is run before running any samples.

8.3.2 Magnetic Sector Mass Spectrometry (High Resolution)

Gas chromatograph parameters and instrument calibration procedures for high resolution mass spectrometry are identical to those employed for low resolution mass spectrometry for analysis of both total Cl_4-Cl_7 dioxins/furans and 2,3,7,8 Cl_4-Cl_7 dioxins/furans. Instrument tuning procedures unique to magnetic sector mass spectrometry are described below.

Total Cl_4-Cl_7

- PFK is used as a reference compound to tune the peak at mass 381 to optimum peak shape and maximum intensity at 1000 resolution. The CVT control is switched to high resolution mode to check the resolution. The peak is re-optimized until the desired resolution is attained.

TCDD/TCDF Only

- Methyl stearate is used on the solid probe as a reference standard to tune the peak at mass 298 to optimum peak shape and maximum intensity at 1000 resolution. The CVT control is switched to high resolution mode to check the resolution. The peak is re-optimized until the desired resolution is attained.

9. QUALITY ASSURANCE PROJECT PLAN

9.1 Introduction

The California Air Resources Board (CARB) has retained ERT, a Resource Engineering Company, to conduct a study of ambient concentrations of chlorinated dibenzodioxins and dibenzofurans within the South Coast Air Basin. This Quality Assurance Project Plan is designed to assure that all sampling and analysis conducted during the course of the program will be completed in a manner which will provide consistent, high-quality data in accordance with the objectives of the sampling and analysis program.

9.2 QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability

9.2.1 Precision, Accuracy, Completeness

The collection and analysis of air samples for the compounds listed in Table 9-1 requires that sampling and analysis procedures be conducted with properly operated and calibrated equipment by competent personnel. The Standard Operating Procedures (SOPs) and Calibration Procedures found in the appendices of this document will assure that the precision, accuracy, and completeness goals listed in Table 9-2 are achieved.

9.2.2 Representativeness and Comparability

The QA objective is that all measurements be representative of the media being sampled. The number and location of monitoring sites, the sampling frequency and sampling duration determined in the monitoring plan will assure representativeness for this program.

TABLE 9-1

LISTING OF PCDD/PCDF ISOMERS SELECTED FOR SAMPLING AND ANALYSIS IN THE SOUTH COAST AIR BASIN

PCDD Isomers	PCDF Isomers
2,3,7,8 TCDD	2,3,7,8 TCDF
1,2,3,7,8 PeCDD	1,2,3,7,8 PeCDF
1,2,3,6,7,8 HxCDD	2,3,4,7,8 PeCDF
1,2,3,7,8,9 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,4,7,8 HxCDD	1,2,3,7,8,9 HxCDF
1,2,3,4,6,7,8 HpCDD	1,2,3,4,7,8 HxCDF
	2,3,4,6,7,8 HxCDF
	1,2,3,4,6,7,8 HpCDF
	1,2,3,4,7,8,9 HpCDF

TABLE 9-2

SUMMARY OF DATA QUALITY GOALS

OBJECTIVES FOR SAMPLE COLLECTION PROCEDURES

MEASUREMENT METHOD	MATRIX	PRECISION (STD.DEV.)	ACCURACY	COMPLETENESS
PCDDs/PCDFs (PS-1 SORBENT SAMPLER)	POLYURETHANE FOAM (PUF)	± 15%	± 85%	95%

OBJECTIVES FOR ANALYTICAL PROCEDURES

MEASUREMENT METHOD	MATRIX	PRECISION (STD.DEV.)	ACCURACY	COMPLETENESS
LOW RESOLUTION GC/MS	POLYURETHANE FOAM (PUF)	± 25%	± 80%	95%
HIGH RESOLUTION GC/MS	POLYURETHANE FOAM (PUF)	± 25%	± 80%	95%

OBJECTIVES FOR COMBINED SAMPLING AND ANALYSIS PROCEDURES

MEASUREMENT METHOD	MATRIX	PRECISION (STD.DEV.)	ACCURACY	COMPLETENESS
PS-1 COLLECTION/ GC/MS ANALYSIS	POLYURETHANE FOAM (PUF)	± 50%	± 60%	90%

In addition, all data resulting from the sampling and analyses should be comparable with information obtained from other similar air monitoring programs. By following the published, standard sampling and analytical methods and procedures found in the appendices of this document, as well as using traceable calibration standards and standard measurement units, comparability will be assured for this program.

9.3 Sample Control and Chain of Custody

9.3.1 General

The purpose of sample control and chain-of-custody procedures is to document the identity of the sample and its handling from the point of collection until analysis and data reduction are completed. Custody records trace a sample from its collection through all transfers of custody until it is transferred to the analytical laboratory. Internal laboratory records then document the custody of the sample through its final disposition.

9.3.2 Sample Control

Sample control will begin in the analytical laboratory, with the preparation of sampling kits. Sampling kits will be provided to the field coordinator by the sample custodian. The sampling kits will be enclosed in coolers, and will include the appropriate sample media, chain-of-custody forms and all appropriate shipping blanks and field blanks. The sample media provided in the sampling kits will be packaged by the sample custodian. Completed sampling kits will be returned to the sample custodian by the field coordinator after the samples have been collected. As samples are collected each sample will be labeled with the following information:

- station location - description of place where sample was taken;
- date - a six-digit number indicating the year, month and day of collection;
- time - the military start time and end time of collection;
- sample number - a unique identification number which may contain the above information, but which distinguishes among samples collected from the same site at the same time;
- sampler - signature of person collecting the sample; and
- remarks - any pertinent field observations or further sample description.

After collection, identification, and preservation, the sample is maintained under chain-of-custody procedures discussed below.

In addition to the labeling of the sample media, a field sample log is maintained by the field coordinator (or designee) in which a complete account is kept of samples collected at each sampling site. The sample log is filled out as soon as possible after sample collection. Information entered in the log for each sample includes:

- sample site location,
- sample ID number,
- sample type,
- date collected,
- start and end time of sample run.

9.3.3 Chain-of-Custody Procedures

Chain-of-custody procedures serve at least two essential purposes in ambient monitoring programs of this nature:

- They provide a formalized mechanism for assignment of responsibility for sample integrity.

- They provide objective, physical evidence of the possession history and integrity of each sample, from collection, through analysis to data reporting, which supports the validity of site investigation data.

A sample is under a person's custody if:

- it is in that person's possession, or
- it is in that person's view, after being in his or her possession, or
- it was in that person's possession and he or she locked it up to prevent tampering, or
- it is in a secure area, under the control of that person.

The following custody procedures are followed in the field:

1. Prior to commencement of sampling, the field coordinator will instruct the sampling team in the chain-of-custody procedures.

2. The field sampler is personally responsible for the care and custody of the samples collected until they are transferred or dispatched properly.

3. The field coordinator determines whether proper custody procedures were followed during the field work and decides if additional samples are required.

4. As soon as each sample has been collected, containerized and labeled, it is entered on the chain-of-custody form (Figure 9-1). One chain-of-custody form may be used for as many as

CHAIN OF CUSTODY RECORD

Client/Project Name	Project Location
Project No.	Field Logbook No.
Sampler: (*Signature*)	Chain of Custody Tape No.

Sample No./ Identification	Date	Time	Lab Sample Number	Type of Sample	ANALYSES							REMARKS

Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received for Laboratory: (*Signature*)	Date	Time
Sample Disposal Method:	Disposed of by: (*Signature*)			Date	Time
SAMPLE COLLECTOR	ANALYTICAL LABORATORY				
				No.	

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Figure 9-1 Typical Chain-of-Custody Record eight samples but all samples sharing a single chain-of-custody form must be packaged and shipped together. The sampler must complete all of the heading information on the form accurately and legibly. For each sample, the following information is entered:

- sample identification number (must be identical to the identification number on the sample label),
- date and military time of sample collection,
- type of sample media,
- analyses to be performed.

The following procedures will be followed in shipping samples and transferring custody:

1. Samples will be packaged properly for shipment (see Section 9.4) and dispatched to ENSECO-CAL in Sacramento, CA laboratory for analysis, with a separate custody record accompanying each package. Shipping containers will be sealed with chain-of-custody tape for shipment to the laboratory. The chain-of-custody seal will be signed and dated by the person applying the tape. The number on the chain-of-custody tape is recorded in the field notebook or on the sample log. The method of shipment, courier name(s) and other pertinent information are entered in the "Remarks" box. A copy of the shipper's waybill or airbill is retained by the last custodian prior to shipment.

9.4 Sample Collection Procedures

The sample collection procedures that will be used for this program can be found in Appendix C to this air quality monitoring plan.

In addition to these sample collection procedures, the following quality control measures will be followed during sample collection.

9.4.1 Sorbent Pretreatment and Quality Control Acceptance Criteria

PUF sorbent cartridges will be prepared and accepted for field use following the procedure found in Appendix E of this document.

9.4.2 Field Biased Blanks

Approximately 10 field-biased blanks will be collected during the course of the program. Field blank cartridges will be cleaned, prepared, and shipped as an actual PUF sorbent cartridge ready for field sampling. Once in the field, the cartridge chosen as the field blank will be removed from the sample jar and opened at the same time and in the same manner as one of the cartridges to be used for sampling. Once sampling has begun, the field blank will be re-sealed in its sample jar, covered with aluminum foil, and left out at the monitoring site near the sampling apparatus. When sampling is completed, the field blank is re-opened while the sampling cartridge is being removed from the sampling system. The field blank is then sealed back in its sample jar at the same time as the sample cartridge, labeled, and returned to the sample cooler and then to the lab for analysis.

Each monitoring day one pair of field blanks will be collected at any one of the selected monitoring sites to provide an indication of typical conditions.

Field blanks will be used to correct samples on an absolute basis.

9.4.3 Collocated Samplers/Field Replicates

Collocated samples will be employed over the course of the monitoring program to assess the precision of the combined sample collection and analysis scheme as well as play a critical role in statistical data analysis.

During each sampling period, at least one of the sampling sites will be collocated. The two collocated samplers will be operated for an identical duration at identical flow rates and will be located close enough to each other so as to represent the same ambient air conditions without causing interferences with each other (approximately 2 meters separation). The collocated site(s) does not necessarily have to be the same site each sampling period.

9.4.4 Surrogate Spikes

Prior to sample collection, polyurethane foam sorbent cartridges will be spiked with Cl^{37}-2,3,7,8-TCDD and C_{13}-2,3,7,8-TCDD at levels 5 to 10 times the arbitrary lower detection limits noted in Table 6-1. Based on the absolute lower limits of detection of 5-10 pg/sample achievable via high-resolution mass spectrometry, it is anticipated that 50 pg of each of the isotopically labeled surrogates will be applied to each sorbent cartridge prior to the commencement of each sample collection period. If logistics permit, the sorbent cartridges may actually be fortified at ENSECO-CAL's laboratory prior to disposition to the ERT field team.

9.5 Analytical Procedures

The analytical procedures that will be used for this program can be found in Appendix F and G to this air quality monitoring plan.

A summary of the more noteworthy features of the laboratory quality control regime are provided in the discussion which follows.

9.5.1 Method Blanks

Method blanks are clean sorbent cartridges that are stored with the samples upon receipt at the laboratory until final analyses. Method blanks are analyzed with the actual samples and are used to correct the samples for spurious laboratory-derived contamination. Detailed instruction on the use of method blanks can be found in the analytical SOPs found in Appendices F and G.

9.5.2 Laboratory Blanks

Blanks used in instrument calibration; these blanks contain the reagents used in preparing instrument calibration standards except the parameters of interest.

9.5.3 Surrogate Compounds

Isotopically labeled surrogate compounds will be fortified into each program sample prior to the conduct of the sample preparation scheme. Isotopically labeled PCDD/PCDF congeners other than the two species selected for field surrogate spiking will be selected by ENSECO-CAL personnel. These components will be selected from those isotopes listed in the ENSECO-CAL SOP provided in Appendixes F and G.

9.6 Data Reduction and Validation

Quality control measures will be used to ensure the generation of reliable data from sampling and analysis activities. All information will be collected and organized clearly and concisely, and reported accurately.

9.6.1 Field Data Reduction

The data collected in the field will be recorded on the appropriate field data sheets and/or in the field logbook, and will be reviewed by at least two field sampling team members. Errors or discrepancies will be noted in the field logbook. All data and calculations will be checked by the project field coordinator or designee and will be signed to demonstrate that the data have been reviewed and approved. All checks and data reviews will be completed before any data are given to the laboratory for calculations. At least 10% of all strip chart data, from meteorological monitoring, will be hand reduced to 1-hour and daily averages, and compared to the corresponding hourly and daily data from the data acquisition system.

9.6.2 Laboratory Analysis Data Reduction

Analysis results will be reduced to the concentration units specified in the respective analytical procedures found in Section 8 and the Appendixes F and G of this air quality monitoring plan, using the equations given in each procedure. All calculations will be recorded in the laboratory notebook, and will be checked and signed by the project laboratory coordinator or designee to demonstrate that the calculations and data have been approved and reviewed. All appropriate blank corrections will be applied to data before it is released from the laboratory.

9.6.3 Data Validation

Data validation is the process of filtering data and accepting or rejecting it on the basis of sound criteria. Validation methods and criteria appropriate to the type of data and the purpose of the measurement will be used in this program. Record of all data will be maintained, even that judged to be an "outlying" or spurious value. The persons validating the data will have sufficient knowledge of the technical work to identify questionable values.

The following criteria will be used to evaluate the field sampling data:

- use of approved test procedure,
- use of properly operating and calibrated equipment, and
- use of materials that have passed QC checks.

The criteria listed below will be used to evaluate the analytical data:

- use of approved analytical procedure,
- use of properly operating and calibrated instrumentation,
- acceptable results from analyses of QC samples,
- precision and accuracy achieved should be comparable to that achieved in previous similar analytical programs.

9.6.4 Identification and Treatment of Outliers

Any data point which deviates markedly from others in its set of measurements will be investigated; however, the suspected outlier will be recorded and retained in the data set while it is investigated. Outliers will be identified by following the procedure for identification and treatment of outliers found in The Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1, Principles, (EPA-600/9-76-005).

Since an outlier may result from unique circumstances at the time of sample analysis or data collection, those persons involved in the analysis and data reduction will be consulted. This may provide an experimental reason for the outlier. Further statistical analyses will be performed with and without the outlier to determine its effect on the conclusions.

In summary, every effort will be made to include the outlying value in the reported data. If the value is rejected, it will be identified as an outlier, reported with its data set and its omission noted.

9.7 Data Reporting

Following all data reduction and validation procedures, results will be reported on all parameters measured.

9.8 Internal Quality Control Checks and Frequency

Quality control checks will be performed to ensure the collection of representative samples and the generation of valid analytical results. The checks will be performed by field and laboratory personnel throughout the program.

9.8.1 Sampling QC Checks

The sampling quality control aspects for this program will include the following:

- field-biased blanks of the collection media;
- collocated samples;
- calibration, orientation and data collection procedures for meteorological monitoring instruments.

9.8.2 Analytical QC Checks

<u>Method Blanks</u>

PUF cartridges prepared at the same time as those used for actual samples. These cartridges will be stored in a clean area of the laboratory until they can be stored with the samples upon their receipt into the laboratory. One method blank will be prepared and analyzed with each set of the samples.

<u>Spiked Samples</u>

Spiked samples are used to measure the recovery efficiency of the analytical regime for the analytes of interest. Blank

PUF cartridges will be spiked at concentrations 5 to 10 times the aforementioned method detection limit of 5 to 10 pg absolute with all the analytes of interest as a measure of accuracy for the analytical procedure.

Surrogate Compounds (GC/MS)

Isotopically labeled (e.g., C_{13} or Cl^{37}) surrogate compounds having similar characteristics as the compounds of interest will be spiked onto each PUF cartridge sample, field sample or quality control sample.

NBS Traceable Standards

National Bureau of Standards (NBS)-traceable samples, which are certified Standard Reference Materials (SRMs) for PCDDs/PCDFs, will be used to verify analytical accuracy. The SRM to be used in this program is SRM #1614 and is certified for 2,3,7,8-TCDD and C_{13}2,3,7,8-TCDD at levels of 98.3 ng/g and 95.6 ng/g, respectively.

9.9 Quality Assurance Performance Audits, System Audits, and Frequency

The quality assurance program will include both performance and system audits as independent checks of the quality of data obtained from sampling, analysis, and data gathering activities. Every effort will be made to have the audit assess the measurement process in normal operation. Either type of audit may show the need for corrective action.

The sampling, analysis, and data handling segments of a project are checked in performance audits. A quality assurance staff member will be present during the performance of these audit operations to ensure the independence of the quantitative results.

9.9.1 Performance Audits

EPA Quality Control Concentrates and NBS Standard Reference Materials will be used to assess the analytical measurement. The laboratory QC coordinator will direct the inclusion in the sample load of QC samples appropriate to the analyses performed in each batch of 20 or fewer samples.

9.9.2 System Audits

A system audit will be conducted at least once during the program to ensure that the elements outlined in the project QA plan are functioning.

9.10 Preventive Maintenance Procedures and Schedules

An orderly program of positive actions to prevent the failure of equipment or instruments used in the sampling and analysis segments of this program will be followed.

9.10.1 Sampling Equipment Preventive Maintenance

Meteorological monitoring equipment used for this program will follow the preventive maintenance recommendations found in the manufacturer's operations manual. All preventive maintenance will be completed before committing the instruments for field use.

PS-1 sampler maintenance will also follow the preventive maintenance procedures recommended by the manufacturer.

9.10.2 Analytical Equipment Preventative Maintenance

Preventive maintenance of all analytical instrumentation will be completed at the laboratory on a regular basis by competent personnel using the manufacturer's recommendations and schedules.

9.11 Specific Routine Procedures Used to Assess Data Precision, Accuracy, Representativeness, Comparability and Completeness

9.11.1 Precision

Precision will be determined by the collection and analysis of replicate or collocated samples. The analysis of the replicate samples collected by the collocated samplers will provide an estimate of overall measurement precision. The analysis of laboratory duplicates (replicate aliquots from one collected sample) will enable the estimation of analytical precision.

Precision will be determined by the collection and analysis of replicate samples and will be expressed as the standard deviation, which is determined according to the following equation:

$$S = \sqrt{\frac{\sum_{i=1}^{N} X_i^2 - \frac{1}{N}\left(\sum_{i=1}^{N} X_i\right)^2}{N-1}}$$

where S = standard deviation

X_i = individual measurement result

N = number of measurements

Relative standard deviation may also be reported. If so, it will be calculated as follows:

$$RSD = 100 \left(\frac{S}{\bar{X}}\right)$$

where RSD = relative standard deviation, expressed in percent

S = standard deviation

X = arithmetic mean of replicate measurements

9.11.2 Accuracy

Accuracy will be estimated from both the analysis of "blind" QC samples where true values are known to the laboratory QC coordinator as well as through the use of isotopically labeled surrogate compounds applied to each and every program sample under field and laboratory conditions. Accuracy will be expressed as percent recovery or as relative error. The formulas to calculate these values are:

$$\text{Percent Recovery} = 100 \left(\frac{\text{Measured Value}}{\text{True Value}} \right)$$

$$\text{Relative Error} = 100 \left(\frac{\text{Measured Value} - \text{True Value}}{\text{True Value}} \right)$$

9.11.3 Completeness

Completeness will be reported as the percentage of all measurements made whose results are judged to be valid. The procedures to be used for validating data and determining outliers were described earlier in this QA plan. The following formula will be used to estimate completeness:

$$C = 100 \left(\frac{V}{T} \right)$$

where C = percent completeness

V = number of measurements judged valid

T = total number of measurements

9.12 Corrective Action

The acceptance limits for the sampling and analyses to be conducted in this program will be those stated in the method or defined by CARB. The corrective actions are likely to be immediate in nature and most often will be implemented by the laboratory or field coordinator. The corrective action will usually involve recalculation, reanalysis, or repeating a sample collection run. The program corrective action policy is described here.

9.12.1 Immediate Corrective Action

Specific operating procedures and checklists are designed to help analysts detect the need for corrective action. Often the person's experience will be more valuable in alerting the operator to suspicious data or malfunctioning equipment.

If a corrective action can be taken at this point, as part of normal operating procedures, the collection of poor quality data can be avoided. Instrument and equipment malfunctions are amenable to this type of action and procedures include troubleshooting guides and corrective action suggestions. The actions taken should be noted in field or laboratory notebooks but no other formal documentation is required, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system.

Corrective action during the field sampling portion of a program is most often a result of equipment failure or an operator oversight and may require repeating or invalidating a sampling session. When equipment is discovered to be defective (i.e., pre-and post-sampling calibration check) it is repaired or replaced and a correction factor will be established. If a correction factor is unacceptable, the run is repeated or invalidated. Operator oversight is best avoided by having field crew members audit each others work before and after a test. Every effort is made by the field coordinator to ensure that all procedures are followed.

Corrective action for analytical work would include recalibration of instruments, reanalysis of known QC samples and, if necessary, of actual field samples.

If the problem is not solved in this way, more formalized long-term corrective action may be necessary.

9.12.2 Long-Term Corrective Action

Any quality problem which cannot be solved by immediate corrective action falls into the category of long-term corrective action. A closed loop corrective action system used for long-term corrective action follows:

- Identify and define the problem.
- Assign responsibility for investigating the problem.
- Investigate and determine the cause of the problem.
- Determine a corrective action to eliminate the problem.
- Assign and accept responsibility for implementing the corrective action.
- Establish effectiveness of the corrective action and implementation.
- Verify that the corrective action has eliminated the problem.

Documentation of the problem is important to the system. When long-term corrective action is necessary, a Request for Corrective Action will be initiated by the person identifying the quality problem. A Request for Corrective Action will be documented in the Corrective Action Log and will include: identification of the problem, possible cause, person responsible for action on the problem, a description of the corrective action planned by the person responsible for action and the date of implementation. Later, the project manager along with the person who identified the quality problem will document that the action has been implemented and its effectiveness. If the corrective action proves to be inadequate, the corrective action loop and Request for Corrective Action will be repeated.

10. DATA INTERPRETATION

10.1 Statistical Analysis Procedures

Given the limited amount of data that will result from the analysis of the collected ambient air samples, the data interpretation effort will focus on answering the following questions in the comparison of various sources of PCDD/PCDF concentration data:

(1) Are the distributions of concentrations measured at background stations, area source stations, and combustion source stations significantly different from each other?

(2) Are the distributions of concentrations measured at background stations significantly different from one station to the next?

(3) Are the distributions of concentrations measured during this program significantly different from the data identified in the cited literature?

(4) In those instances where the sample was analyzed to distinguish the PCDDs and PCDFs associated with the particulate and vapor phases, are the distributions statistically comparable to the data identified in the cited literature?

Since the underlying concentration frequency distributions are unknown and the number of observations is relatively small, these analyses will be carried out by use of non-parametric statistical tests. The first two types of analyses described above will be performed using the Wilcoxon Rank Sum Test, which is designed to determine whether the underlying populations of two independent samples are centered differently. To illustrate the application of this test, consider the following sets of concentrations measured at two sites:

Site 1 (4 observations)	Site 2 (6 observations)
6.1	11.0
8.0	8.1
7.3	10.4
7.1	9.0
	8.2
	7.6

The concentrations from both sites are then combined and sorted in ascending order, with the site identity of each concentration being retained. Each sorted concentration is then ranked and the sum of the ranks computed for each site as shown below:

Combined Ordered Concentrations			Combined Ranks	
Site 1	Site 2		Site 1	Site 2
6.1			1	
7.1			2	
7.3			3	
	7.6			4
8.0			5	
	8.1			6
	8.2			7
	9.0			8
	10.4			9
	11.0			10
		Rank Sums	11	44

The next step in the analysis is to determine the probability that a rank sum of 11 or smaller would be obtained if the four Site 1 samples were drawn randomly from the group of ten samples from Sites 1 and 2 combined. In this case there is only a 1 percent probability that the underlying populations of concentrations at Sites 1 and 2 could be identical. If n is the number of observations for the larger sample and m is the number of observations for the smaller sample, then, for $n > 7$, the distribution of rank sums is approximately normal with the mean and variance given by $(1/2)m(m+n+1)$, respectively. For smaller values of n, the cumulative frequency distributions of rank sums have been tabulated.

10.2 Particulate-Associated Versus Vapor Phase Concentrations

In most cases during the course of this program, the particulate filter and its associated sorbent cartridge will be combined prior to analysis. In these cases, each data point will represent ambient concentrations for both particulate-associated and vapor phase PCDDs/PCDFs combined. However, due to the differential health effects and diversity of atmospheric behavior associated with particulate-associated organics in comparison to vapor phase organics, it would be useful to CARB to conduct a limited number of analyses of the particulate filter separate from its associated sorbent cartridge.

Approximately 10 to 12 sets of collocated samples are expected to be collected during the course of this program. Of these, approximately one-half (5 to 6) will be selected for particulate versus vapor phase analyses. The data obtained from this portion of the study will be compared statistically, as described in sub-section 10.1 (above) to the particulate versus vapor phase data in the cited literature. Note that these data represent operationally defined partitioning and not actual partitioning of PCDDs/PCDFs in ambient air.

10.3 Comparison of Source Data Categories (Background, Area, Combustion)

All data collected as a result of the sampling and analysis portions of this program will be statistically compared, as described in sub-section 10.1 (above), to assess the significance of PCDD and PCDF concentrations in relation to source categories. This will allow conclusions to be drawn as to the impact of current sources on existing PCDD/PCDF levels in the South Coast Air Basin.

10.4 Comparison to Ambient PCDD/PCDF Data Identified in the Literature Search

The data collected as a result of the sampling and analysis portions of this program will also be statistically compared, as described in subsection 10.1 (above), to data collected in other ambient air PCDD/PCDF studies identified in the literature search. This data will help CARB assess the significance of the existing levels of PCDDs and PCDFs in the South Coast Air Basin in relation to other geographical areas.

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APPENDIX A

AMBIENT MONITORING OF SEMI-VOLATILE ORGANICS USING HIGH-VOLUME SORBENT SAMPLERS

BIBLIOGRAPHY

AMBIENT MONITORING OF SEMI-VOLATILE ORGANICS USING HIGH VOLUME SORBENT SAMPLERS - CRITICAL QUALITY CONTROL FEATURES AND OTHER CONSIDERATIONS IN SAMPLE COLLECTION AND NETWORK DESIGN

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AMBIENT MONITORING OF SEMIVOLATILE ORGANICS EMPLOYING HIGH-VOLUME SORBENT SAMPLERS - SOME CRITICAL FEATURES OF THE SAMPLE COLLECTION PROCESS AND NETWORK DESIGN

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